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Molecular Structure of Some Sulfur-substituted Schiff Bases of 1,2-Diamines with Two Molecules of Acetylacetone and Their Metal Complexes as Obtained from Absorption and Circular Dichroism Spectra and from X-Ray Diffraction Methods

H. P. JENSEN,[a] B. SAUSTRUP KRISTENSEN,[a] H. MOSBÆK[a] and I. SØTOFTE[b]

[a] Chemistry Department A, Building 207 and [b] Chemistry Department B, Building 301, Technical University of Denmark, DK-2800 Lyngby, Denmark

The Schiff base condensation products between one molecule of 1,2-diamines and two molecules of acetylacetone where the oxygen atoms have been substituted with sulfur and their metal complexes were studied by absorption and circular dichroism spectroscopy and by X-ray diffraction methods.

Only when the spatial separation between the chromophoric groups of the dimers is small exciton splitting in the electronic spectra is observed, and in the case of optically active dimers the associated Cotton effect may then be used to study rotational conformers around the substituted ethylene bridge linking the two monomeric parts together.

The crystal structure of the compound 4,4′-(*R*,*R*-$(-)_D$-1,2-cyclohexanediimine)di(3-penten-2-thione) has been determined in two different crystalline modifications. Both modifications are orthorhombic, space group $P\,2_12_12_1$. Mod 1: $a=12.403(3)$ Å, $b=16.567(2)$ Å, $c=17.833(1)$ Å, $Z=8$. Mod 2: $a=10.255(5)$ Å, $b=13.210(3)$ Å, $c=13.304(2)$ Å, $Z=4$. The structures have been refined to an R value of 0.085 and 0.072, respectively. The two crystallographically independent molecules of Mod 1 and the molecule of Mod 2 are not significantly different. The angle between two thioacetylacetone planes is about 80°. The absolute configuration of the molecule has been determined. The S – S distances in the molecules are 6.0 – 6.4 Å.

Through UV absorption and circular dichroism spectroscopy it has been possible within an exciton formalism to study rotational conformations around the substituted ethylene bridge in various Schiff base condensates of one molecule of 1,2-diamines and two molecules of β-diketones (ONNO).[1-3] Furthermore it has been possible to use the formalism in the case of neutral complexes of Cu^{2+}, Ni^{2+} and VO^{2+} assigning ligand field transitions and absolute configurations,[4] one of which [4,4′-(*R*-propylenediiminato)di(3-penten-2-one)copper(II)] was confirmed by X-ray structural analysis.[5]

This tempted us to investigate optically active sulfur analogous of ONNO, the oxygen atoms of the Schiff bases being substituted with sulfur (=SNNS).[6-8] The fact that equivalent distributions between the tautomers I, II and III of Fig. 1 have been found for the monomeric parts (ON and SN) of the dimers ONNO and SNNS,[6,9,10] the most abundant being represented by tautomer III, suggests large structural similarities. Hence it seems reasonable to assume an essentially unpertubed polarisation of the $\pi\rightarrow\pi^*$ transition dipole moment within the planar chromophore SN as compared to the case of ON or acetylacetone (OO), *i.e.* only

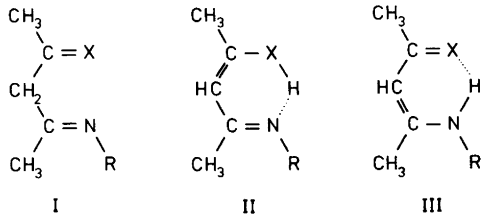

Fig. 1. Tautomeric forms of Schiff base condensate and S-substituted derived from amine and acetylacetone. X = O or S.

slightly off the sulfur-nitrogen direction. This conclusion has been confirmed through an extended Hückel calculation using orbital ionization energies for the diagonal elements and the Wolfsberg-Helmholtz approximation for the off-diagonal elements.[11] In both ON and SN the $\pi\rightarrow\pi^*$ transition dipole moment is found to be polarized some 10° off the nitrogen-chalcogen direction.

If there is no electron transfer or orbital overlap between the two chromophores in a dimer the excited states of the two halves interact only though a coupling of electronic motions resulting in a splitting of the $\pi\rightarrow\pi^*$ transition band inversely proportional with the spatial separation of the two chromophores to the third power (Eqn. 6 of Ref. 1), *i.e.*, when the separation is small (~ 3 Å)[1-4] we observe a splitting in the UV absorption, and in the case of optically active dimers these should furthermore exhibit circular dichroism with rotatory strengths of opposite signs for the two transitions; accordingly it is possible from the sign of the rotatory strength of, *e.g.*, the low energy component to assign an absolute configuration (Δ or Λ)[12] in terms of chirality of the $\pi\rightarrow\pi^*$ transition dipole moments contained in the two chromophore planes.[1,13]

When the spatial separation is big (6–7 Å), however, exciton splitting is expected to be negligible. This was observed with the species tn(acacH)$_2$,[1] tn(fmcH)$_2$[2] or *R*-1,3-bn(fmcH)$_2$,[2] and in the case of optically active dimers, as, *e.g.*, the two latter compounds, it is only possible to observe the inherent Cotton effect from the presumed $n\rightarrow\pi^*$ transitions.

EXPERIMENTAL

Schiff bases of diamines and acetylacetone (ratio 1:2) were prepared in analogy with the procedures given by McCarthy *et al.*[14] and converted to thiones according to Wei *et al.*[7,8] and Gerlach and Holm.[6] Diamines were obtained and resolved as described in the experimental sections of Refs. 2 and 15. UV absorption spectra were measured with a Cary 14 spectrophotometer, and circular dichroism spectra with a Roussel-Jouan dichrograph II and a Jobin-Yvon dichrograph III. ^{13}C NMR spectra were recorded at 22.63 MHz with a Bruker WH 90. The identities of the prepared compounds were established through chemical analyses.

When recrystallized from methanol *R*-chxn-(SacacH)$_2$ exists in two different modifications. Mod 1 appears when the compound is dissolved in methanol at 50 °C and then rapidly cooled to 0 °C. Mod 2 appears when the compound is dissolved in methanol at 20 °C and the solution is allowed to evaporate slowly at room temperature.

Molar absorptions and circular dichroisms in Figs. 5–8 are given in units of 1000 cm^2/mol.

Abbreviations

Amines. ma = methylamine, *R*-pn = (*R*)-(−)$_D$-1,2-propanediamine, *S*-pn = (*S*)-(+)$_D$-1,2-propanediamine, *R*-chxn = *trans*-(*R*,*R*)-(−)$_D$-1,2-cyclohexanediamine, tn = 1,3-propanediamine, *R*-1,3-bn = (*R*)-(−)$_D$-1,3-butanediamine, *S*-stien = (*S*,*S*)-(−)$_D$-1,2-diphenyl-1,2-ethanediamine. Assignments of absolute configurations of optically active diamines are according to Gillard[16] and Balieu *et al.*[17]

Diones. acacH = acetylacetone (2,4-pentanedione), fmcH = formylcamphor (3-formyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) obtained from natural (+)$_D$-camphor.

Condensates. ma(acacH)(4-methylimino-3-penten-2-one) *etc.* symbolizes condensates of an amine with acetylacetone. ma(SacacH)(4-methylimino-3-penten-2-thione) *etc.* symbolizes compounds where the oxygen atoms in the acetylacetone condensates have been substituted with sulfur.

CRYSTAL DATA

4,4′-(*R*,*R*-(−)$_D$-1,2-cyclohexanediimine)di(3-penten-2-thione); $C_{16}H_{26}N_2S_2$; M = 310.5. Orthorhombic. Systematic absences: *h*00 when *h* odd, 0*k*0 when *k* odd, 00*l* when *l* odd; space group $P2_12_12_1$ (No. 19).

Mod 1: $a = 12.403(3)$ Å, $b = 16.567(2)$ Å, $c = 17.833(1)$ Å. $V = 3664$ Å^3. $Z = 8$. $D_c = 1.13$ g cm^{-3}, $D_o = 1.15$ g cm^{-3} (flotation). $F(000) = 1344$.

Mod 2: $a = 10.255(5)$ Å, $b = 13.210(3)$ Å, $c = 13.304(2)$ Å. $V = 1802$ Å^3. $Z = 4$. $D_c = 1.14$ g cm^{-3}, $D_o = 1.15$ g cm^{-3} (flotation). $F(000) = 672$.

$\mu(\mathrm{MoK}\alpha) = 2.8$ cm^{-1}, $\mu(\mathrm{CuK}\alpha) = 25.7$ cm^{-1}.

X-RAY TECHNIQUE

Lattice type and space group were established from photographs taken with Cu*K*α and Mo*K*α radiation. Intensities were measured by a ω scanning technique on an Enraf Nonius CAD-4-F diffractometer. Graphite monochromated Mo*K*α radiation was used. Harmonics were excluded by means of a pulse height discriminator. Reflections with $\sin\theta/\lambda \leqslant 0.53$ Å^{-1} were measured for both

modifications. For Mod 1 the 5054 reflections measured were reduced to 1423 independent observed reflections which had $I > 2\sigma(I)$, where $\sigma(I)$ is calculated from counting statistics. For Mod 2 2566 reflections were reduced to 1131 independent observed reflections. The dimensions of the crystals used were $0.07 \times 0.16 \times 0.27$ mm and $0.15 \times 0.15 \times 0.30$ mm for Mod 1 and Mod 2, respectively. No correction for absorption was applied. The following computer programmes were used: programmes written at Chemistry Department B for processing the diffractometer output, MULTAN[18] and the X-RAY system[19] for the crystal structure analysis, and ORTEP II[20] for the illustrations. All calculations were carried out on an IBM 370/165 computer situated at the Technical University of Denmark.

The atomic scattering factors used were those of Cramer and Mann.[21] The anomalous dispersion corrections to the scattering factor of the sulfur atom were those of Cramer and Liebermann.[22]

STRUCTURE DETERMINATION

For Mod 1 the multiple-tangent-formula method, MULTAN, failed to solve the structure even after changing the starting point. Therefore the coordinates for the four sulfur atoms were deduced from the three-dimensional Patterson function. The positions of the remaining nonhydrogen atoms were derived from successive Fourier syntheses. For Mod 2 the coordinates of all nonhydrogen atoms except two were determined using MULTAN. The position of the last two carbon atoms were found in a Fourier map. The structures were refined by full least-squares minimization of $\Sigma w(|F_o| - c|F_c|)^2$. With anisotropic temperature factors and for Mod 1 use of the weighting scheme[23] $w^{-1} = 16.397 - 0.723|F| + 0.015|F|^2 - 1.640 \sin\theta/\lambda$, the refinement resulted in $R = 0.085$ ($R_w = 0.086$). For Mod 2 the weighting scheme used was $w^{-1} = 4.122 - 0.148|F| + 0.006|F|^2 - 5.348 \sin\theta/\lambda$, and the refinement resulted in $R = 0.072$ ($R_w = 0.078$). Hydrogen atoms have not been included in the structure determinations. The asymmetric carbon atoms in the $(-)_D$-1,2-cyclohexanediamine part of the ligand is known to have the *R*-configurations.[16] Even though the anomalous dispersion correction of the scattering factor of sulfur is small with Cu$K\alpha$ radiation, the absolute configuration of Mod 1 was confirmed by comparison of the observed and calculated intensity differences (Table 1). The reflections used were $4kl$ and $4\bar{k}l$ collected on a semiautomatic equi-inclination diffractometer (Stoe & Cie, Darmstadt, DBR).

Table 1. Observed and calculated structure amplitudes of Bijvoet pairs.

h k l	$F_c(hkl)$	Observed relations	$F_c(h\bar{k}l)$
4 1 9	483	>	455
4 3 3	430	>	418
4 4 1	160	<	190
4 4 2	334	>	316
4 5 2	422	<	449
4 5 3	449	>	430
4 8 1	418	>	396
4 8 5	463	<	475
4 11 6	187	<	208

The final positional parameters and their estimated standard deviations are listed in Table 2 (labelling of the atoms is given in Fig. 2). The final thermal parameters and their estimated standard deviations and a list of observed and calculated structure factors may be obtained from the authors on request.

DESCRIPTION OF THE STRUCTURES

Bond lengths and bond angles together with estimated standard deviations are listed in Tables 3 and 4. By inspection of the tables it is apparent that there are only minor differences between the two independent molecules of Mod 1 and between molecules of Mod 1 and 2. The standard deviations are rather large due to the small number of

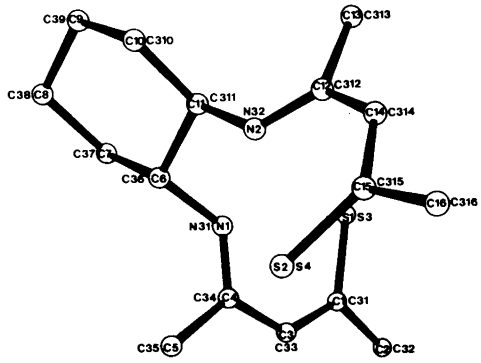

Fig. 2. Mod 2 viewed along the *b*-axis. The labelling inside the atoms corresponds to Mod 2 and one of the molecules in Mod 1. The labelling outside the atoms refers to the atoms of the other molecule of Mod 1.

Table 2. Atomic coordinates. The estimated standard deviations are given in parenthesis.

Atom	Mod 1			Mod 2		
	z	*y*	*z*	*x*	*y*	*z*
S1	0.1773(5)	0.5131(3)	0.4931(3)	0.6943(3)	0.0196(3)	0.6293(3)
S2	0.6798(5)	0.6093(3)	0.4898(4)	0.7468(3)	0.4870(3)	0.5442(2)
N1	0.3561(11)	0.5615(8)	0.5941(8)	0.8930(9)	0.1792(6)	0.6078(6)
N2	0.5442(11)	0.4766(9)	0.5475(9)	0.8068(10)	0.3503(6)	0.7157(6)
C1	0.1698(18)	0.6137(12)	0.4943(11)	0.7145(11)	0.0402(8)	0.5028(9)
C2	0.0744(18)	0.6567(15)	0.4542(11)	0.6352(12)	−0.0283(10)	0.4342(10)
C3	0.2446(16)	0.6632(11)	−0.5368(11)	0.7975(11)	0.1118(7)	0.4608(9)
C4	0.3313(15)	0.6385(11)	0.5817(10)	0.8862(12)	0.1787(8)	0.5090(8)
C5	0.3981(16)	0.7051(12)	0.6200(12)	0.9684(12)	0.2480(9)	0.4475(9)
C6	0.4351(14)	0.5334(10)	0.6481(10)	0.9861(12)	0.2391(8)	0.6685(9)
C7	0.3732(16)	0.5141(12)	0.7223(10)	1.0934(13)	0.1700(9)	0.7091(10)
C8	0.4547(18)	0.4788(14)	0.7803(11)	1.1827(14)	0.2277(10)	0.7806(11)
C9	0.5044(20)	0.4030(12)	0.7493(11)	1.1050(16)	0.2733(10)	0.8668(11)
C10	0.5618(17)	0.4174(12)	0.6756(13)	0.9950(13)	0.3432(9)	0.8274(10)
C11	0.4849(15)	0.4555(11)	0.6171(9)	0.9077(12)	0.2832(8)	0.7571(8)
C12	0.5633(15)	0.4292(11)	0.4903(12)	0.6956(12)	0.3740(8)	0.7601(8)
C13	0.5100(18)	0.3491(11)	0.4825(12)	0.6528(13)	0.3212(9)	0.8579(9)
C14	0.6335(15)	0.4574(11)	0.4323(10)	0.6078(12)	0.4459(8)	0.7210(9)
C15	0.6879(15)	0.5334(13)	0.4277(12)	0.6231(10)	0.5009(8)	0.6309(9)
C16	0.7676(20)	0.5377(15)	0.3580(13)	0.5184(11)	0.5811(9)	0.6055(11)
S3	−0.2355(5)	0.7997(4)	0.8731(3)			
S4	0.2225(5)	0.7649(3)	0.7761(3)			
N31	−0.0920(14)	0.8992(10)	0.7798(10)			
N32	0.1007(11)	0.8886(9)	0.8607(9)			
C31	−0.2547(17)	0.7712(11)	0.7824(14)			
C32	−0.3383(18)	0.6992(13)	0.7692(14)			
C33	−0.2050(16)	0.8038(13)	0.7189(13)			
C34	−0.1239(14)	0.8645(12)	0.7143(14)			
C35	−0.0798(20)	0.8876(17)	0.6397(12)			
C36	−0.0152(14)	0.9654(10)	0.7785(10)			
C37	−0.0723(16)	1.0506(12)	0.7668(12)			
C38	0.0102(18)	1.1194(12)	0.7765(15)			
C39	0.0612(18)	1.1170(16)	0.8495(14)			
C310	0.1263(16)	1.0394(12)	0.8596(13)			
C311	0.0437(15)	0.9653(11)	0.8564(11)			
C312	0.1277(14)	0.8577(12)	0.9283(12)			
C313	0.0877(16)	0.8902(15)	0.9976(12)			
C314	0.1957(15)	0.7869(12)	0.9293(12)			
C315	0.2439(17)	0.7427(12)	0.8699(12)			
C316	0.3148(20)	0.6724(12)	0.8895(15)			

observed reflections. For Mod 1 the ratio number of observations to number of variables is about four and for Mod 2 about six. Therefore the data do not permit a close comparison of bond lengths and bond angles or a discussion of the bond character of the C−C bonds and the C−N bonds, however, it is apparent that the bonds are not localized. The thioacetylacetonimine parts are nearly planar with angles between the two planes in the molecule of 85 and 80° for the two independent molecules in Mod 1. In Mod 2 the angle is 80°. For Mod 1, molecule 1, the angles between a plane through four atoms of the cyclohexane ring (C7, C8, C10, C11) and the two chromophoric parts are 66 and 84°. The corresponding angles for molecule 2 are 57 and 80° and for Mod 2, 77 and 77°. The bond lengths and angles and the planarity of the chromophoric parts are in agreement with the

results obtained for 4,4'-(*R*-propylenediiminato)di-(3-penten-2-one)copper(II).[5]

For Mod 1 the S–S distances in the two molecules are 6.433(9) and 5.966(9) Å, respectively. However, there are shorter S–S distances between the molecules, *viz* S1(x,y,z)–S3($-x,-\frac{1}{2}+y,\frac{3}{2}-z$) of 4.324(8) Å and S2($x,y,z$)–S4($\frac{1}{2}+x,\frac{3}{2}-y,1-z$) of 5.207(9) Å. For Mod 2 the S–S distance in the molecule is 6.300(5) Å and between S1(x,y,z) and

Table 3. Bond lengths in Å. The estimated standard deviations are given in parenthesis.

	Mod 1	Mod 2
S1–C1	1.67(2)	1.717(12)
C1–C2	1.56(3)	1.521(17)
C1–C3	1.45(3)	1.390(16)
C3–C4	1.40(3)	1.421(16)
C4–C5	1.54(3)	1.490(17)
C4–N1	1.33(2)	1.317(14)
N1–C6	1.45(2)	1.480(15)
C6–C7	1.56(3)	1.529(18)
C6–C11	1.53(3)	1.542(16)
C7–C8	1.56(3)	1.524(20)
C8–C9	1.50(3)	1.521(21)
C9–C10	1.51(3)	1.548(20)
C10–C11	1.55(3)	1.517(17)
C11–N2	1.48(2)	1.470(15)
N2–C12	1.31(3)	1.321(15)
C12–C13	1.49(3)	1.540(16)
C12–C14	1.43(3)	1.408(16)
C14–C15	1.43(3)	1.411(16)
C15–C16	1.59(3)	1.546(16)
C15–S2	1.68(2)	1.724(12)
S3–C31	1.70(3)	
C31–C32	1.60(3)	
C31–C33	1.40(3)	
C33–C34	1.43(3)	
C34–C35	1.49(3)	
C34–N31	1.36(3)	
N31–C36	1.45(2)	
C36–C37	1.59(3)	
C36–C311	1.57(3)	
C37–C38	1.54(3)	
C38–C39	1.45(4)	
C39–C310	1.53(3)	
C310–C311	1.60(3)	
C311–N32	1.46(2)	
N32–C312	1.35(3)	
C312–C313	1.44(3)	
C312–C314	1.46(3)	
C314–C315	1.42(3)	
C315–C316	1.50(3)	
C315–S4	1.73(2)	

Table 4. Bond angles (°). The estimated standard deviations are given in parenthesis.

	Mod 1	Mod 2
S1–C1–C3	122.3(16)	125.1(9)
S1–C1–C2	119.6(17)	115.4(8)
C2–C1–C3	117.9(17)	119.4(11)
C1–C3–C4	128.6(18)	129.3(11)
C3–C4–N1	123.5(17)	119.2(10)
C3–C4–C5	117.3(17)	119.8(10)
C5–C4–N1	119.2(16)	121.0(10)
C4–N1–C6	125.1(14)	125.6(9)
N1–C6–C7	107.3(14)	109.7(9)
N1–C6–C11	107.6(14)	106.4(9)
C11–C6–C7	109.3(14)	109.3(10)
C6–C7–C8	108.7(15)	110.8(10)
C7–C8–C9	109.5(16)	110.8(11)
C8–C9–C10	112.4(16)	111.2(11)
C9–C10–C11	111.0(17)	109.1(10)
C10–C11–N2	110.7(15)	109.4(9)
C10–C11–C6	110.4(14)	111.1(10)
C6–C11–N2	107.7(14)	107.9(9)
C11–N2–C12	126.9(15)	125.6(9)
N2–C12–C13	121.8(18)	121.1(10)
N2–C12–C14	118.6(16)	123.1(10)
C13–C12–C14	119.5(17)	115.8(10)
C12–C14–C15	128.0(17)	126.1(11)
C14–C15–C16	112.2(18)	117.4(10)
C14–C15–S2	126.4(16)	126.6(9)
C16–C15–S2	121.3(16)	116.0(9)
S3–C31–C33	127.0(16)	
S3–C31–C32	116.0(17)	
C32–C31–C33	117.0(20)	
C31–C33–C34	129.0(21)	
C33–C34–N31	117.0(20)	
C33–C34–C35	119.4(21)	
C35–C34–N31	123.5(18)	
C34–N31–C36	119.7(16)	
N31–C36–C37	112.4(15)	
N31–C36–C311	106.8(14)	
C311–C36–C37	108.9(14)	
C36–C37–C38	110.2(16)	
C37–C38–C39	111.8(19)	
C38–C39–C310	111.1(20)	
C39–C310–C311	107.6(16)	
C310–C311–N32	110.8(14)	
C310–C311–C36	109.2(15)	
C36–C311–N32	105.9(14)	
C311–N32–C312	119.9(18)	
N32–C312–C313	122.6(18)	
N32–C312–C314	117.5(18)	
C313–C312–C314	119.8(19)	
C312–C314–C315	131.0(19)	
C314–C315–C316	118.3(19)	
C314–C315–S4	123.1(16)	
C316–C315–S4	118.6(16)	

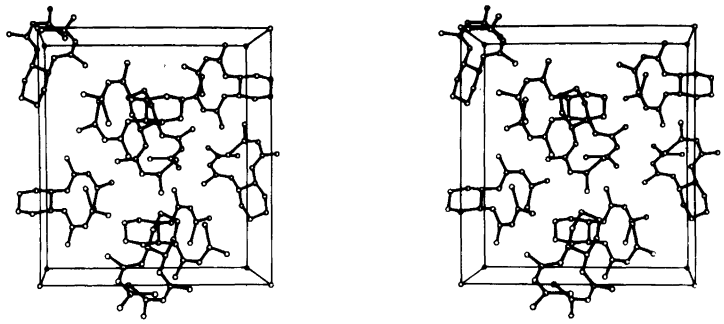

Fig. 3. Stereo view along the *a*-axis of the structure of Mod 1.

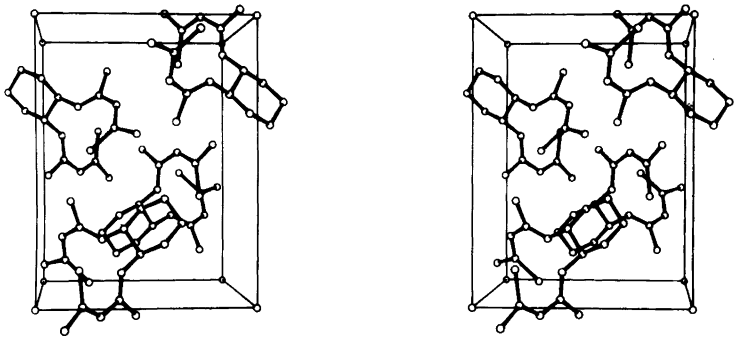

Fig. 4. Stereo view along the *b*-axis of the structure of Mod 2.

S2($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$) there is a shorter S–S distance of 5.138(5) Å. The packing of a unit cell is shown for Mod 1 in Fig. 3 and for Mod 2 in Fig. 4. All intermolecular distances are larger than the sum of the van der Waals radii[24] of the atoms. The shortest distance between two carbon atoms is in both structures 3.53 Å.

SPECTROSCOPIC RESULTS AND DISCUSSION

The basis for adopting the exciton model to the Schiff bases of acetylacetone was the observation of a splitting in the UV absorption of, *e.g.*, *R*-chxn-(acacH)$_2$ correlated with circular dichroism bands of opposite signs.[1] However, the S-substituted 1,2-cyclohexanediamine derivatives show no splitting in the $\pi\rightarrow\pi^*$ transition region and only a single circular dichroism band (Fig. 5). In order to investigate whether tautomerisation occurs during the dissolution process we have, for *R*-chxn(SacacH)$_2$, measured the absorption and circular dichroism spectra of microcrystals suspended in KBr matrices, and the ^{13}C NMR spectrum in $CDCl_3$ solution. From the facts that the electronic spectra (Abs and CD) are equal in KBr and in $CHCl_3$, and that the ^{13}C NMR spectra show 8 peaks (*R*-chxn(SacacH)$_2$

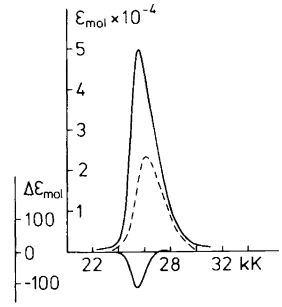

Fig. 5. Molar absorption and circular dichroism in $CHCl_3$ of *R*-chxn(SacacH)$_2$ (———) and ma(SacacH) (– – –).

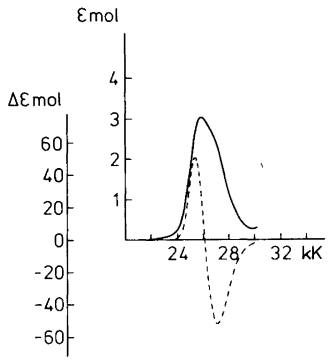

Fig. 6. Molar absorption (———) and circular dichroism (– – –) in CH_3OH of *S*-stien(SacacH)$_2$.

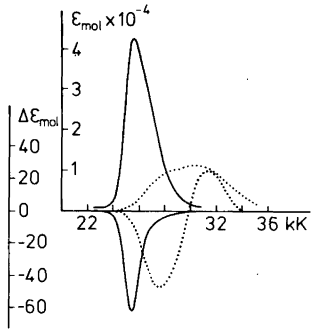

Fig. 7. Molar absorption and circular dichroism in $CHCl_3$ of *R*-pn(SacacH)$_2$ (———) and Zn *S*-pn(Sacac)$_2$ (. . .).

contains 16 C atoms), it is concluded that no tautomerisation occurs.

Since a dimer shows a dipole strength twice that of a monomer (Fig. 5) and no exciton splitting as a consequence of the above demonstrated large spatial separation of the two chromophoric parts, the observed Cotton effect may be identified as due to an $n \rightarrow n^*$ transition. This assignment is in accordance with the observation that ε_{max} is found at another wavelength than $\Delta\varepsilon_{max}$ (388 nm and 392 nm) showing that the two bands may have different causes, the absorption being mainly $\pi \rightarrow \pi^*$.

In the case of either bulky substituents on the ethylene bridge of the Schiff base condensates, or complexation, it should be possible to minimize the spatial separation of the two monomeric parts of the dimer, SNNS, with exciton coupling as a result.

These situations are demonstrated by *S*-stien(SacacH)$_2$ (Fig. 6) which, from the sign of the low energy component in the Cotton effect, may be assigned the same absolute configuration as *S*-chxn(acacH)$_2$,[1] and by Zn *S*-pn(Sacac)$_2$ (Fig. 7) which from a similar argumentation may be assigned the same absolute configuration as Cu *S*-pn(acac)$_2$ (the mirror image of Fig. 2 in Ref. 4). The intensity of the $\pi \rightarrow \pi^*$ transition band in the complex is somewhat reduced compared with the free ligand, but the reduction is comparable with findings in the case of pn(acacH)$_2$ and its Cu^{2+} complex.[4]

For the sake of further comparison we have prepared Cu *R*-pn(Sacac)$_2$ electronic spectra of which are shown in Fig. 8, exhibiting a profound similarity with the spectra of Cu *R*-pn(acac)$_2$ (Fig. 1 of Ref. 4). This similarity means that the model presented in Ref. 4 and further investigated in Refs. 5

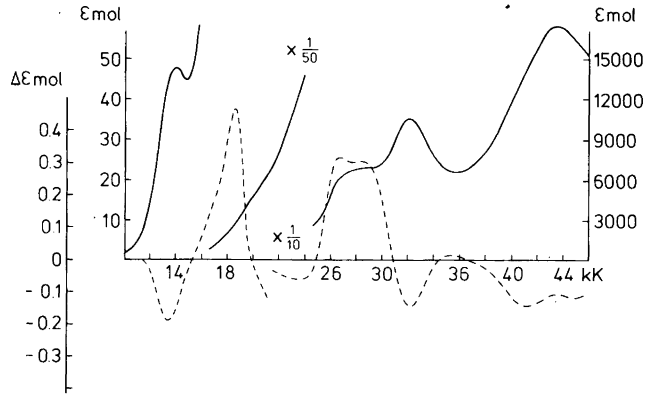

Fig. 8. Molar absorption (———) and circular dichroism (– – –) in CH_3OH of Cu *R*-pn(Sacac)$_2$.

and 25 for assignments of electronic transitions in Cu *R*-pn(acac)$_2$ may also be valid for Cu *R*-pn(Sacac)$_2$. Consequently the structure in solution of the two copper complexes is the same (Fig. 2 of Ref. 4) as seen from the signs of the Cotton effects associated with the high energy exciton components. This structural assignment is supported by the similarities in signs and positions of the ligand field transitions of the two complexes.

The only major difference between the two sets of spectra is found in the 25 – 26 kK region. This is. however, the region where we expect to find transitions originating in σ^n(non-bonding chalcogen orbitals)$\rightarrow\pi^*$,[5,25] and therefore differences are quite eligible and actually support the given interpretation of bands in this region.

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