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The Molecular Structure of 4,4′-(*R*-Propylene-diiminato)-di-(3-penten-2-one)copper(II) Studied by X-Ray Diffraction Methods and Circular Dichroism

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Absorption and circular dichroism spectra of the title compound have been measured for the complex dispersed in KBr discs. The interpretation of these spectra by the molecular exciton theory showed that the complex is tetrahedrally distorted with the absolute configuration *Λ*. These conclusions have been confirmed by determination of the crystal structure by X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$, $Z=8$, with unit cell dimensions $a=12.452$ Å, $b=21.032$ Å and $c=10.766$ Å. The final least squares refinement using 2521 observed reflections gave unit weighted and weighted residuals of 0.047 and 0.058, respectively.

The two crystallographically independent molecules in the structure are not significantly different and have a tetrahedrally distorted planar coordination of the copper(II) atoms. The angle between the two acetylacetone planes is 10° with the absolute configuration *Λ*. The *R*-propylene part of the ligand has its methyl group in an axial position and the ethylene bridge in a *gauche* conformation.

The stereochemical results from the structure determination are in qualitative agreement with the exciton interpretation of the solid state circular dichroism spectra.

Transition metal complexes of the condensation products between diamine and conjugated dioxo compounds have received great attention and work has been done using a variety of techniques. Currently there is great interest in the ability of cobalt(II) complexes to reversibly bind molecular oxygen. If such systems are to be used as models for biological oxygen carriers it is desirable to obtain knowledge about all the factors which influence molecular and electronic structures. The crystal and molecular structures of ethylenebis (acetylacetoneiminato)copper(II) and a series of adducts have been determined.[1–4] It was found that the complex as a whole deviates only slightly from planarity. Jensen and Larsen[5] found that the title compound, also called *R*-propylenebis(acetylacetoneiminato) copper(II), [Cu *R*-pn(acac)$_2$], in solution is very distorted and they estimated by means of the exciton theory that the two acetylacetonato parts form an angle of some 40°.

This geometry of the complex including the absolute configuration of [Cu *R*-pn(acac)$_2$] was used within a simple MO scheme to combine ligand π-orbitals with metal $3d$ orbitals and thus explaining the signs of the rotatory strengths of the $d-d$ transitions. The exciton model as applied to such complexes is a very crude model which only considers the weak coupling of the π-transitions on the two acetylacetone parts of the ligand and ignores the presence of the copper ion. Therefore, it is of importance to obtain independent information about the structure and also to measure the absorption and circular dichroism under conditions where the structure is known.

EXPERIMENTAL

Crystallographic examination. The title compound was prepared[5] from Cu(OH)$_2$ and the acid form of the ligand in acetone and recrystallized from cyclohexane to obtain single crystals

suitable for the X-ray diffraction studies. The crystals grow as red-brown rhombic plates. In polarized light they appear red and green when the electric vector is parallel to the two rhombic diagonals.

Preliminary photographs showed that the crystals are orthorhombic. The space group is uniquely determined to be $P2_12_12_1$ from the systematically absent reflections. A single crystal of the dimensions $0.29 \times 0.36 \times 0.15$ mm^3 was chosen for the data collection and for the accurate determination of the unit cell parameters. The reflections from the crystal were very broad, so to get good resolution of the diffraction peaks, Cu$K\alpha$ radiation obtained from a graphite monochromator was used for the data collection on a Picker FACS-1 diffractometer. The setting angles for 12 relatively high angle reflections were located automatically on the diffractometer and these angles were used in a least squares refinement to determine the cell parameters. The density of the crystals was determined by flotation in a mixture of chlorobenzene and bromobenzene.

The intensity data were measured at 22 °C by a $\theta - 2\theta$ scan performed at a rate of 1° per minute. The scan range was increased with 2θ. Background counts were made for 20 s at each end of the scan range. The intensities of three standard reflections were measured after every 40 reflections. These measurements indicated that no deterioration or misalignment of the crystal had occurred during the data collection.

The 4039 reflections with $\sin\theta/\lambda \leq 0.580$ measured during the data collection were reduced to 2521 independent observed reflections which had $I/\sigma(I) > 1.5$, where $\sigma(I)$ is the standard deviation of the intensity calculated from counting statistics. The data set was corrected for Lorentz and polarization effects but not for absorption.

The following computer programs were employed during this work: The Vanderbilt System [6] for all diffractometer operations, a local modification of the program NRC-2A[7] for data reduction, ORTEP II [8] for illustrations and The X-RAY System [9] for the crystal structure analysis.

The atomic scattering factors used in the calculations were those of Cromer and Mann.[10] The anomalous dispersion corrections to the scattering factor of the copper atom were by Cromer and Liebermann.[11]

Spectral measurements. The circular dichroism spectra were obtained on Roussell-Jouan dichrographs I and II and absorption spectra were recorded on a Cary 14 spectrophotometer. [Cu *R*-pn(acac)$_2$] was treated in a ball mill with KBr for 2 – 5 h. For measurements in the UV region various dilutions were made. The KBr-complex mixture was pressed into plates by standard techniques used for IR spectroscopy. Plate thickness was measured by micrometer. The plates for UV measurements were sufficiently dilute to be completely transparent to the eye whereas the KBr-suspensions for visible spectra invariably gave turbid plates due to the relatively high complex concentration (2×10^{-2} – 10^{-3} mol/dm^3). The visible absorption of many plates was measured and qualitative equality with solution spectra was found. The experimental shortcomings exclude quantitative comparisons in this region. The UV absorption of the plates indicated little disturbance from internal reflections. The circular dichroism measurements on KBr-disks were performed on a number of plates of varying complex concentrations ($2 \times 10^{-2} - 10^{-5}$ M) and widths (1 – 2 mm). Maximum uncertainties on UV measurements are estimated to ± 10 % judged as the reproducibility of independent measurements.

CRYSTAL DATA

4,4′-(*R*-Propylenediiminato)di(3-penten-2-one)copper(II); $C_{13}H_{20}N_2O_2Cu$; M = 299.9. Orthorhombic, $a = 12.452(6)$ Å, $b = 21.032(12)$ Å, $c = 10.766(7)$ Å, $U = 2819(5)$ Å^3. $D_m = 1.41 \pm 0.02$ g cm^{-3}, $Z = 8$, $D_c = 1.413(3)$ g cm^{-3}. μ(Cu$K\alpha$) = 21.2 cm^{-1}, $F(000) = 1256$. Systematically absent reflections: $h00$ when h odd, $0k0$ when k odd, $00l$ when l odd; space group $P2_12_12_1$ (D_2^4, No. 19). Developed faces {010} and {101}.

STRUCTURE DETERMINATION AND REFINEMENT

The coordinates for the two independent copper atoms could be deduced from the three-dimensional Patterson function. The positions of the other non-hydrogen atoms of the structure were determined from two successive Fourier syntheses phased from the partial structure.

This structure has been refined by the method of least squares minimizing $R = \sum w(|F_o| - K|F_c|)^2$ using the 2521 observed reflections.

Initially a unit weighted full matrix refinement of the scalefactor, the atomic coordinates and individual, isotropic temperature factors was performed. Later when anisotropic temperature factors were introduced the parameters were varied in blocks corresponding to the two independent molecules. The weights employed during the last cycles of least squares refinement were of the form $w = X \cdot Y$. The

two factors X and Y in the product are defined as follows, for $\sin\theta > 0.4700$ $X=1.0$ otherwise $X=\sin\theta/0.4700$, for $|F_o|<15.0$ $Y=1.0$ otherwise $Y=15.0/|F_o|$.

The asymmetric carbon atom in the amine part of the ligand has previously been shown to have the *R*-configuration,[12] and this was used to decide between the two possible enantiomeric structures. Though the anomalous dispersion correction to the scattering factor of copper is small with Cu$K\alpha$ radiation the absolute configuration was confirmed by least squares refinement. Refinement of the structure corresponding to the *R*-configuration of the asymmetric carbon atom converged when the unit weighted and weighted residuals were 4.7 and 5.8 %, respectively, while the refinement of the mirror image of the structure corresponding to the *S*-configuration of the carbon atom converged when the equivalent residuals were 4.8 and 6.0 %. Application of Hamiltons *R*-factor test [13] to these results indicates that the structure corresponding to the *S*-configuration can be rejected at a level of significance of 0.005. No attempt was made to locate the hydrogen atoms in the structure.

Table 1. Final atomic coordinates. The estimated standard deviations × 10^4 are given in parentheses. The first number in the numerical label distinguishes between the two molecules in the structure. The other numbers in the label are illustrated in Fig. 1.

Atom	x	y	z
Cu1	0.59326(0.6)	0.48096(0.3)	−0.01492(0.6)
O11	0.5458(4)	0.4109(2)	−0.1140(4)
C11	0.5687(5)	0.3523(3)	−0.0942(6)
C12	0.6281(5)	0.3297(3)	0.0038(7)
C111	0.5250(8)	0.3065(4)	−0.1908(8)
C13	0.6721(5)	0.3654(3)	0.1006(6)
C131	0.7312(9)	0.3287(5)	0.1999(9)
N11	0.6632(4)	0.4273(2)	0.1053(4)
C14	0.7057(5)	0.4646(3)	0.2109(5)
C15	0.7428(4)	0.5296(3)	0.1600(6)
C151	0.8520(4)	0.5231(4)	0.0940(7)
N12	0.6606(4)	0.5512(2)	0.0713(4)
C16	0.6461(5)	0.6115(3)	0.0479(6)
C161	0.7075(6)	0.6629(3)	0.1175(8)
C17	0.5708(5)	0.6330(3)	−0.0433(6)
C18	0.5104(5)	0.5949(3)	−0.1199(5)
C181	0.4328(6)	0.6258(3)	−0.2096(7)
O12	0.5117(3)	0.5346(2)	−0.1227(3)
Cu2	0.40468(0.6)	0.49875(0.3)	0.24570(0.6)
O21	0.4548(4)	0.4300(2)	0.3473(4)
C21	0.4383(4)	0.3705(3)	0.3264(6)
C22	0.3836(5)	0.3459(3)	0.2271(7)
C211	0.4855(7)	0.3267(3)	0.4238(8)
C23	0.3364(5)	0.3804(3)	0.1296(6)
C231	0.2859(8)	0.3445(4)	0.0217(9)
N21	0.3367(4)	0.4429(2)	0.1275(4)
C24	0.2896(5)	0.4788(3)	0.0237(5)
C25	0.2526(4)	0.5439(3)	0.0699(5)
C251	0.1458(5)	0.5394(4)	0.1394(7)
N22	0.3371(3)	0.5671(2)	0.1541(4)
C26	0.3550(5)	0.6278(3)	0.1691(6)
C261	0.2959(6)	0.6778(3)	0.0935(7)
C27	0.4295(5)	0.6524(3)	0.2584(6)
C28	0.4861(4)	0.6152(3)	0.3436(5)
C281	0.5595(6)	0.6489(3)	0.4336(6)
O22	0.4840(3)	0.5547(2)	0.3531(4)

The final coordinates and anisotropic thermal parameters for the non-hydrogen atoms in the structure are listed in Tables 1 and 2, respectively. A list of observed and calculated structure amplitudes with phases may be obtained from the authors upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Table 3 lists the bond lengths and bond angles for the two crystallographically independent molecules. By inspection of the table it is apparent that there are only minor differences between the molecules. The average numerical difference in the bond lengths is 0.92 and in the bond angles it is 1.24 measured in units of the estimated standard deviation from the least squares refinement. A normal probability plot of the ranked deviates in bond lengths and bond angles shows that these follow a normal distribution. Therefore it is concluded that the structure contains two not significantly different molecules. Some average values of important bond lengths and bond angles are shown in Fig. 1.

It is of interest to compare the conformation of the bridging propylene group with the conformation found for the corresponding complexes derived from ethylenediamine. Hall and Waters have determined the crystal structure for ethylenebis(acetylacetoneiminato) copper(II),[1] [Cu en(acac)$_2$], where the ethylene bridge takes an unsymmetric *gauche* conformation. A *gauche* conformation is likewise found for the hemihydrate,[2] whereas eclipsed conformations were found for the hydrate [3] and

Table 2. The thermal parameters, U_{ij}, in units of $Å^2 \times 10^4$. The expression for the temperature factor is $\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$. The estimated standard deviations from the least squares refinement are given in parentheses. The labelling is the same as in Table 1.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	472(4)	470(4)	466(4)	8(3)	−34(3)	−7(3)
O11	859(28)	511(22)	602(24)	30(21)	−189(22)	−63(19)
C11	601(33)	486(28)	623(33)	−21(26)	66(28)	−41(26)
C12	733(38)	488(29)	862(45)	39(27)	145(37)	109(33)
C111	1201(64)	574(37)	882(50)	−72(42)	−36(51)	−174(37)
C13	519(30)	639(35)	650(35)	−43(28)	1(28)	221(30)
C131	1143(65)	1001(60)	937(57)	121(55)	−186(55)	437(51)
N11	454(23)	639(28)	497(24)	−41(21)	−10(20)	88(21)
C14	523(31)	815(40)	481(28)	−49(29)	−57(25)	14(28)
C15	399(27)	789(38)	567(30)	−75(27)	−38(24)	−91(30)
C151	391(27)	964(47)	818(42)	16(32)	91(30)	49(41)
N12	426(23)	565(25)	554(25)	10(20)	−28(21)	−60(21)
C16	497(28)	594(33)	677(36)	−89(26)	157(28)	−160(29)
C161	802(45)	620(37)	1009(54)	−176(36)	1(44)	−248(39)
C17	539(31)	481(26)	699(35)	0(24)	77(28)	−4(26)
C18	537(30)	554(31)	521(30)	22(25)	77(27)	60(25)
C181	845(46)	686(37)	736(41)	124(36)	−55(37)	213(33)
O12	591(21)	476(20)	536(21)	6(17)	−96(19)	18(17)
Cu2	414(3)	540(4)	406(3)	−57(3)	−28(3)	−22(3)
O21	613(22)	536(22)	522(21)	−15(18)	−75(20)	−8(18)
C21	406(26)	617(33)	578(32)	4(24)	71(25)	−27(27)
C22	631(36)	565(32)	789(42)	16(28)	16(34)	−97(31)
C211	865(47)	634(38)	800(40)	104(35)	−43(41)	113(36)
C23	457(29)	631(34)	611(35)	−63(26)	14(28)	−199(29)
C231	989(54)	858(49)	923(55)	−142(46)	−170(52)	−383(46)
N21	462(25)	684(30)	449(24)	−88(22)	7(21)	−73(22)
C24	549(30)	805(38)	465(27)	−120(30)	−64(26)	7(30)
C25	386(28)	716(36)	493(28)	−124(24)	−47(24)	87(27)
C251	402(28)	919(48)	744(40)	−71(30)	101(30)	146(37)
N22	380(22)	561(26)	485(23)	−74(19)	−45(20)	51(21)
C26	481(28)	651(36)	574(33)	13(27)	−8(28)	47(28)
C261	800(46)	627(36)	800(45)	−94(34)	−164(41)	101(34)
C27	522(30)	584(30)	601(32)	−69(24)	−12(29)	−66(28)
C28	482(28)	596(33)	481(28)	−96(25)	35(26)	−86(26)
C281	771(41)	773(40)	582(35)	−227(35)	−111(33)	−126(32)
O22	632(23)	549(22)	512(20)	−95(19)	−104(20)	10(18)

the methylammonium perchlorate adduct.[4] In [Cu en(acac)$_2$].$CH_3NH_3ClO_4$ the ethylene carbon atoms are co-planar with the four ligating atoms whereas in [Cu en(acac)$_2$].H_2O these atoms are situated on one side of the plane of the ligators. An ORTEP drawing of [Cu *R*-pn(acac)$_2$] (Fig. 2) shows the *gauche* conformation of the ethylene bridge with the methyl group in the axial position. The dihedral angle defined by N1, C4, C5, and N2 is 42.3(6)° and 41.5(6)° for the two molecules. This conformation is surprisingly close to the conformation determined [14] by ^{1}H NMR for the corresponding diamagnetic complex [Ni *R*-pn(acac)$_2$]. In most cases chelate rings of 1,2-propanediamine have the methyl group in an equatorial position, but in [Cu *R*-pn(acac)$_2$] this would lead to a severe interaction with the methyl group on the nearest acetylacetone part. The conformation of the Cu−pn ring is δ as also proposed by Downing and Urbach [14] on the basis of the circular dichroism of the $d-d$ transitions. A similar conformation was found by X-ray diffraction for the salicylaldimine complex [Cu pn(sal)$_2$].[15]

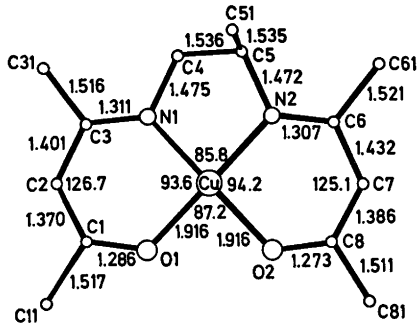

Fig. 1. An ORTEP drawing viewed perpendicular to the mean coordination plane. The shown bond lengths and bond angles are mean values for the two independent molecules of the asymmetric unit.

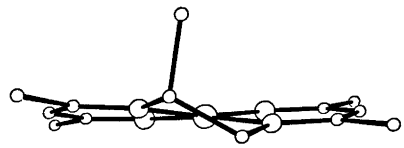

Fig. 2. The molecule viewed along the molecular pseudo two-fold axis.

To illustrate the overall geometry of [Cu *R*-pn(acac)$_2$] Table 4 lists the distances of the atoms from some characteristic planes. The complex is grossly planar but with a significant tetrahedral distortion as may be seen from the distribution of atoms above and below the plane (I) defined by the four ligators. The two acetylacetoneimine parts are nearly planar with the angle between the planes of 10 and 11° for the two molecules.

Table 3. Bond lengths (Å) and bond angles (°). The labelling corresponds to Fig. 1. Standard deviations in parentheses in terms of the last digit.

	1	2		1	2
Cu–O1	1.913(4)	1.918(4)	O1 –Cu–O2	87.2(2)	87.2(2)
Cu–O2	1.910(4)	1.922(4)	O1 –Cu–N1	93.6(2)	93.5(2)
Cu–N1	1.925(5)	1.928(5)	N1 –Cu–N2	85.9(2)	85.7(2)
Cu–N2	1.935(5)	1.936(5)	O2 –Cu–N2	94.1(2)	94.3(2)
O1–C1	1.283(7)	1.289(7)	Cu –O1–C1	125.3(4)	125.5(4)
C1–C2	1.373(10)	1.368(9)	O1 –C1–C2	125.4(6)	125.7(6)
C2–C3	1.397(10)	1.405(10)	O1 –C1–C11	114.5(6)	114.0(5)
C3–C31	1.510(11)	1.522(11)	C11–C1–C2	120.0(6)	120.3(6)
C3–N1	1.307(8)	1.315(8)	C1 –C2–C3	126.8(6)	126.6(6)
N1–C4	1.479(8)	1.470(8)	C2 –C3–N1	122.0(6)	121.9(6)
C4–C5	1.543(10)	1.529(9)	C2 –C3–C31	116.4(6)	119.1(6)
C5–C51	1.540(8)	1.529(8)	C31–C3–N1	121.6(6)	118.9(6)
C5–N2	1.472(7)	1.472(7)	Cu –N1–C3	126.6(4)	126.7(4)
N2–C6	1.307(8)	1.306(8)	Cu –N1–C4	111.5(4)	111.3(4)
C6–C7	1.430(9)	1.433(9)	N1 –C4–C5	107.7(5)	109.5(5)
C7–C8	1.375(8)	1.397(9)	C4 –C5–N2	107.1(5)	106.3(4)
C8–C81	1.513(10)	1.509(9)	C51–C5–C4	110.5(6)	111.4(5)
C8–O2	1.269(7)	1.277(7)	C51–C5–N2	110.0(5)	109.9(5)
C6–C61	1.521(10)	1.520(10)	C5 –N2–Cu	112.1(4)	112.3(4)
C1–C11	1.519(10)	1.514(10)	C6 –N2–Cu	126.1(4)	126.1(4)
			N2 –C6–C7	122.0(5)	123.1(6)
			N2 –C6–C61	121.7(6)	121.9(6)
			C61–C6–C7	116.3(5)	115.0(6)
			C6 –C7–C8	125.8(5)	124.4(6)
			C7 –C8–O2	126.3(5)	127.0(5)
			C7 –C8–C81	118.8(5)	117.7(6)
			C81–C8–O2	115.0(5)	115.4(5)
			C8 –O2–Cu	125.6(4)	124.9(4)

Table 4. Distances in Å of the atoms from the least squares planes.[a]

Atom	I		II		III	
	1	2	1	2	1	2
Cu	−0.02	0.01	0.08	0.00	−0.02	−0.10
O1	0.12*	0.11*	0.00*	0.01*	0.26	0.05
N1	−0.12*	−0.11*	0.00*	−0.00*	−0.25	−0.37
O2	−0.12*	−0.11*	−0.04	−0.19	0.01*	0.00*
N2	0.12*	0.11*	0.44	0.24	−0.02*	−0.01*
C1	0.20	0.24	0.00*	0.01*	0.32	−0.03
C2	0.15	0.02	0.01*	0.01*	0.15	−0.25
C11	0.37	0.25	0.00	0.02	0.61	0.15
C3	−0.02	−0.11	−0.01*	−0.01*	−0.14	−0.44
C31	−0.09	−0.31	−0.04	−0.12	−0.32	−0.79
C4	−0.36	−0.28	−0.08	−0.04	−0.62	−0.61
C5	0.36	0.41	0.75	0.65	0.10	0.15
C51	1.87	1.92	2.25	2.17	1.58	1.63
C6	0.15	0.04	0.55	0.18	0.02*	0.01*
C61	0.33	0.17	0.91	0.42	−0.09	0.11
C7	−0.01	−0.12	0.34	0.08	−0.01*	−0.01*
C8	−0.13	−0.16	0.06	−0.23	−0.01*	0.00*
C81	−0.31	−0.31	−0.17	−0.47	−0.07	0.00

[a] The displacements marked with an asterisk are those of the atoms used in determining the least squares plane.

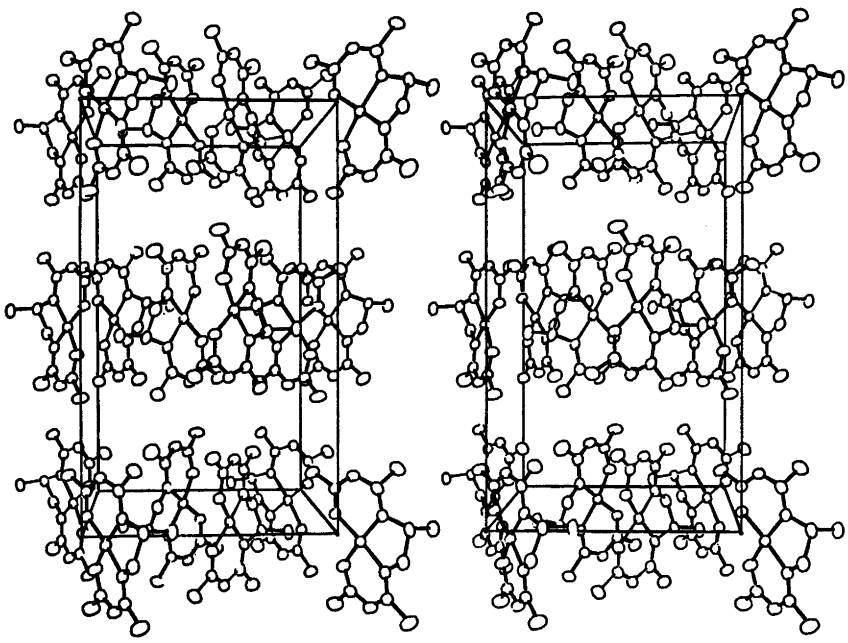

Fig. 3. Stereo pair of the packing viewed along the *c* axis.

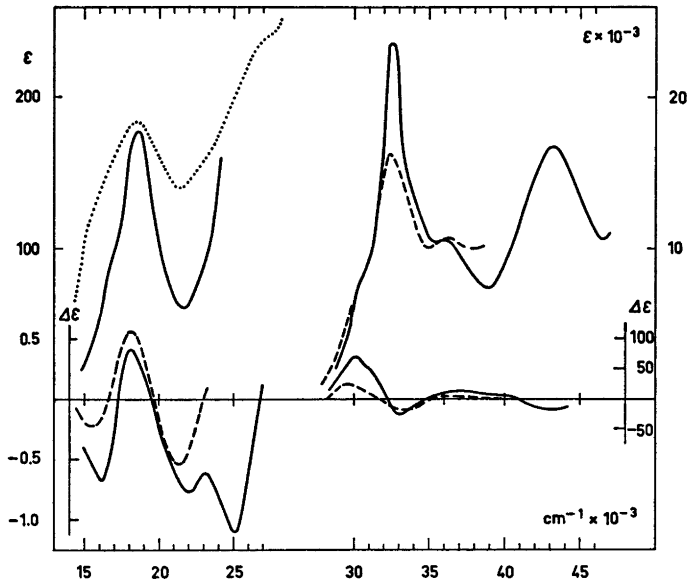

Fig. 4. Absorption and circular dichroism spectra of [Cu *R*-pn(acac)$_2$] in methanol solution (———) and dispersed as crystals in KBr-discs (- - -).

The absolute configuration of the two lines connecting N and O within an acetylacetoneimine is *Λ* thus confirming the qualitative result based on the circular dichroism spectrum of the crystalline compound dispersed in KBr.

The bond lengths and bond angles of the two conjugated acetylacetoneiminato parts differ only insignificantly indicating that the propylene methyl group interacts weakly with the rest of the molecule. All the molecular dimensions are similar to those found for other acetylacetoneiminato complexes. The C–C bond length closest to the nitrogen atom is greater than the C–C distance adjacent to the oxygen atom. This difference is rationalized by assuming that the inner complex is derived from the tautomer form of the ligand where the hydrogen atom is bonded to the nitrogen atom. This is the tautomer found by ^{1}H NMR for the free ligand in solution.[16,17] However, judged by the low value of the C–N bond length, 1.31 Å, it is evident that the conjugation is quite extensive.

The molecular packing in the crystal is determined by van der Waals interactions between adjacent complexes. The two independent molecules are nearly co-planar (angle ~2°) and parallel to the *b* axis. The packing is illustrated in Fig. 3 by a stereo pair seen from the *c* axis. There are only negligible interactions between molecules in the direction of the *b* axis with the shortest distance of 3.9 Å between two methyl carbon atoms.

The complex has earlier been claimed to be more tetrahedrally distorted in solution than found here for the crystalline state.[5] This difference could possibly be a consequence of the packing forces.

SPECTRAL RESULTS AND DISCUSSION

The absorption and circular dichroism spectra of [Cu *R*-pn(acac)$_2$] in methanol [5] are shown in Fig. 4 together with the circular dichroism curve obtained from the complex dispersed in KBr discs. The latter technique has severe limitations as described in the experimental section and only for allowed transitions in the region 29 000 – 34 000 cm^{-1} are the measurements on KBr discs considered truly quantitative. The two circular dichroism curves for this region do show interesting similarities and differences. Firstly, it is noticed that the two Cotton effects attributed to the exciton coupled internal $\pi \rightarrow \pi^*$ transitions have the same sign in solution and in KBr.

This shows that in the complex the acetylacetonate units are distributed with the same absolute configuration in methanol solution and in the solid. The absolute configuration predicted [5] from the chiroptical properties is in agreement with this X-ray diffraction study. Secondly, it is noteworthy that the solution Cotton effects are considerably larger than for the crystalline state. This effect may be explained by a difference in the angle between the two acetylacetonate planes. A larger angle ($\sim 40°$) was earlier estimated for solution conformation compared to the angle found for the complex in crystals ($\sim 10°$).

It is unfortunate that the spectral results of the visible region are too disturbed by internal reflections to be of quantitative use. Instead single crystal linear and circular dichroism measurements can be done giving additional information on the polarization effects.[18]

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