

# Stability of the Nickel(II) Complexes of $N^1$ -Isopropyl-2-methyl-1,2-propanediamine in Aqueous Sodium Perchlorate Solutions and the Crystal Structure of Bis( $N^1$ -isopropyl-2-methyl-1,2-propanediamine)nickel(II) Perchlorate

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The nickel(II) complex formation of  $N^1$ -isopropyl-2-methyl-1,2-propanediamine (=L) has been studied by emf titrations at 25 °C and at total ionic strengths of about 0.04, 0.05, 0.09, 0.5, 1.0 and 2.0. The complex species found were  $NiL^{2+}$  and  $NiL_2^{2+}$ . The absorption maximum at 450 nm suggested the latter to be a planar yellow complex, which was verified by X-ray crystal structure analysis.

$[Ni(C_7H_{18}N_2)_2](ClO_4)_2$  is monoclinic, space group  $P2_1/c$ , with  $a=20.399(12)$ ,  $b=15.026(4)$ ,  $c=16.670(10)$  Å,  $\beta=111.79(4)^\circ$ ,  $Z=8$ . Final  $R=0.061$  for 3650 unique reflections. The coordination sphere of the two independent nickel(II) ions is distorted square-planar with Ni–N distances of 1.900(7)–1.959(7) Å. Complex cations and perchlorate ions form through hydrogen bonding two nonequivalent chains parallel to the  $b$  axis.

The nickel(II) complex formation of  $N$ -alkylated ethylenediamines has been widely studied in our laboratory.<sup>1,2</sup> The main species formed were  $NiX^{2+}$ ,  $NiX_2^{2+}$  and  $NiX_3^{2+}$ , with X denoting the bidentate neutral diamine ligand. We have also found that  $C$ -alkyl-substituted ethylenediamines, with increased sodium perchlorate concentration and temperature, favour the formation of square-planar nickel(II) biscomplexes, where only species  $NiX^{2+}$  and  $NiX_2^{2+}$  appear.<sup>3–6</sup> In this work the tendency of  $N^1$ -isopropyl-2-methyl-1,2-propanediamine to form nickel(II) complexes has been studied with the aid of potentiometric titrations and a crystal structure determination of

the yellow nickel(II) complex precipitated at a pH of about 8.5.

## EXPERIMENTAL

**Reagents.**  $N^1$ -Isopropyl-2-methyl-1,2-propanediamine from Aldrich Chemical Co., Inc. was neutralized with 1 M  $HClO_4$ . An 0.1 M solution was prepared and was analyzed potentiometrically. The other chemicals,  $Ni(ClO_4)_2 \cdot 6H_2O$ ,  $NaClO_4$  and  $NaOH$ , and their analysis were the same as before.<sup>7</sup>

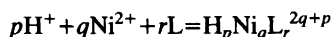
**Solution measurements and calculations.** Radiometer digital pHM52 and pHM64 potentiometers were used for the emf measurements. An electrode system consisting of a Beckman glass electrode of type E and calomel electrode with J-shape liquid junction was tested using two buffers and by means of  $E_o$ -titrations. In ionic strengths 0.04, 0.05 and 0.09 the measured pH values were converted to values of  $-\log h$  by means of apparent  $pf_{H^+}$  values.<sup>8,9</sup> These two methods proved to be in good agreement with each other.

The equilibrium study involved a series of titrations carried out in aqueous solutions at 25 °C and total ionic strengths about 0.04, 0.05, 0.09, 0.5, 1.0 and 2.0 ( $NaClO_4$  as background electrolyte). In the solutions with 0.5 M  $NaClO_4$  as background electrolyte, the establishment of equilibria (6–15 min) was followed with a sensitive REC 61 servograph recorder from Radiometer. The spectra of the complexes were recorded with a Perkin-Elmer model 402 spectrophotometer.

Table 1. Initial concentrations of ligand (*L*) and metal (*M*) with ionic strengths (*I*),  $-\log h$  and  $\bar{n}$  ranges and titration points used in the final calculations.

<i>I</i> average	<i>M</i> : <i>L</i>	<i>L</i> mmol dm <sup>-3</sup>	<i>M</i> mmol dm <sup>-3</sup>	$-\log h$ range	$\bar{n}$ range	Number of points
0.040	1:6	14.3	2.4	6.5–8.8	0.1–1.95	67
	1:4	14.3	3.6			
	1:3	14.3	4.8			
	1:2	14.3	7.2			
0.051	1:2	16.6	8.2	6.6–8.1	0.1–1.4	22
0.088	1:4	33.1	8.2	5.3–8.0	0.01–1.8	56
0.533	1:2	5.5	2.7	5.6–8.5	0.02–1.91	121
	1:4	10.9	2.7			
	1:2	10.9	5.5			
	1:4	16.4	4.1			
1.032	1:4	10.0	2.6	6.2–8.1	0.03–1.5	91
	1:3	10.1	3.4			
	1:2	10.1	5.0			
2.030	1:4	17.5	4.4	6.7–7.5	0.1–1.0	52
	1:4	8.7	2.2			

The initial concentrations of metal and ligand, *M* and *L*, with the ranges of  $-\log h$  and apparent  $\bar{n}$  values can be seen in Table 1. The calculation procedure was the same as described in Ref. 7. The overall stability constant for the reaction



is here defined as

$$\beta_{pqr} = [\text{H}_p\text{Ni}_q\text{L}_r] h^{-p} m^{-q} l^{-r}$$

where *h*, *m*, *l* denote the free concentrations of proton, metal and ligand, respectively.

The program MINIQUAD 75<sup>10</sup> was adapted for calculations. The values for the protonation constants  $\beta_{101}$  and  $\beta_{201}$  were obtained from the results in Ref. 11.

**Crystal preparation and data collection.** The reddish-yellow crystals used for structure determination were obtained by slow evaporation of ethanol solution containing nickel(II) perchlorate and *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine in molar ratio 1:2. Weissenberg photographs showed the crystals to be identical with the poor quality ones separated from titrated solutions.

Lattice parameters were obtained from least-squares refinement of 23 well-centered reflections measured on a Syntex P2<sub>1</sub> diffractometer using graphite monochromatized MoK $\alpha$  radiation ( $\lambda=0.71069$  Å). Crystal data: *a*=20.399(12), *b*=15.026(4), *c*=16.670(10) Å,  $\beta=111.79(4)^\circ$ , *V*=4744(4) Å<sup>3</sup>, *Z*=8, space group P2<sub>1</sub>/c, *D*<sub>m</sub>=1.45(1), *D*<sub>c</sub>=1.45 g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha)=10.9$

cm<sup>-1</sup>, *F*(000)=2192, crystal dimensions 0.30×0.35×0.50 mm.

Intensity data were collected ( $5 < 2\theta < 45^\circ$ ) at room temperature using the  $\omega$ -scan technique and a scan rate varying from 2.5 to 30.0° min<sup>-1</sup> depending upon the peak intensity. The intensity of one check reflection, recorded after every 99 measurements, remained essentially constant throughout the data collection. Out of 6197 independent reflections measured, 3650 had  $I > 3\sigma(I)$  and were used in the structure determination. The data were corrected for Lorentz and polarization factors.

**Structure determination and refinement.** The structure was solved by a combination of direct and Fourier methods using programs MULTAN 78<sup>12</sup> and XRAY 76.<sup>13</sup> The function minimized in least-squares refinement was  $\Sigma w(|F_o| - |F_c|)^2$  with  $w=1/\sigma^2(F_o)$ . Scattering factors for the non-hydrogen atoms were from Cromer and Mann<sup>14</sup> and for H atoms from Stewart, Davidson and Simpson.<sup>15</sup> Anomalous dispersion corrections were included for Ni and Cl.<sup>16</sup> Isotropic refinement of the model led to an *R* value of 0.108 ( $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ). Refinement with anisotropic temperature factors for non-hydrogen atoms and fixed isotropic ones for geometrically positioned H atoms ( $U_{\text{iso}}=0.07$  Å<sup>2</sup> and X-H=1.0 Å) gave the *R* value 0.061. The average shift/error ratio in the last cycle was 0.04. The largest peak on the final difference map had a density of 0.65 eÅ<sup>-3</sup> near by O24 (B).

It is apparent that perchlorate groups are undergoing considerable thermal motion and

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and the equivalent isotropic temperature factors<sup>a</sup> with e.s.d.'s in parentheses.

Unit A				Unit B			
x	y	z	$B_{\text{eq}}(\text{\AA}^2)$	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Ni (A)	4320(1)	1796(1)	2317(1)	3.29(5)	Ni (B)	2070(1)	3.49(5)
N11	3364(3)	2200(4)	1637(4)	4.2(3)	N11	8319(3)	5.0(4)
N12	3975(3)	1570(4)	3219(4)	4.2(3)	N12	8941(3)	5.2(4)
C11	2910(4)	2062(6)	2147(5)	4.5(4)	C11	7876(4)	5.3(4)
C12	3207(4)	1328(5)	2788(5)	3.7(4)	C12	8350(4)	4.2(4)
C13	3155(4)	415(6)	2340(5)	5.3(5)	C13	8634(4)	6.1(5)
C14	2858(4)	1261(6)	3444(5)	5.4(5)	C14	7934(5)	6.7(6)
C15	3310(4)	3127(6)	1255(5)	4.3(4)	C15	3082(4)	5.3(5)
C16	3614(5)	3818(6)	1918(7)	7.6(6)	C16	3866(7)	7.0(6)
C17	2581(5)	3340(6)	673(6)	6.7(5)	C17	2863(7)	7.3(6)
N21	5275(3)	1398(4)	2978(3)	3.6(3)	N21	2685(4)	4.5(4)
N22	4609(3)	1831(4)	1350(4)	3.8(3)	N22	10226(3)	4.5(4)
C21	5686(4)	1395(6)	2401(5)	4.7(4)	C21	9634(4)	5.4(4)
C22	5198(4)	1203(5)	1486(4)	3.8(4)	C22	10680(4)	4.6(4)
C23	4915(4)	257(6)	1371(5)	5.6(5)	C23	10502(4)	4.2(4)
C24	5557(4)	1394(6)	842(5)	5.1(4)	C24	10758(5)	5.9(5)
C25	5653(4)	1863(7)	3824(5)	4.8(5)	C25	10292(4)	4.9(5)
C26	5658(5)	2856(7)	3708(6)	6.6(6)	C26	9973(5)	6.1(5)
C27	6371(4)	1488(8)	4292(5)	7.1(6)	C27	11057(4)	5.6(5)
C11	3143(1)	3913(2)	4233(2)	5.2(1)	C11	8439(2)	6.1(2)
O11	3730(3)	3391(6)	4268(5)	10.1(5)	O11	8917(6)	16.3(8)
O12	3124(4)	3922(6)	5042(4)	12.1(6)	O12	8031(8)	19.9(9)
O13	3226(4)	4797(5)	4037(6)	12.3(6)	O13	8721(7)	18.1(9)
O14	2527(3)	3597(5)	3623(5)	10.1(4)	O14	8103(5)	16.9(9)
C12	4783(1)	-920(1)	4000(1)	4.7(1)	C12	9269(1)	5.1(1)
O21	4183(4)	-814(6)	4227(5)	11.4(6)	O21	9831(3)	8.0(4)
O22	4998(5)	-89(5)	3883(5)	11.7(6)	O22	8925(5)	15.1(7)
O23	4579(4)	-1413(5)	3241(4)	8.7(5)	O23	9539(5)	15.3(7)
O24	5319(3)	-1377(4)	4675(4)	6.5(4)	O24	8825(5)	18.3(8)

<sup>a</sup> $B_{\text{eq}} = 8/3 \pi^2 \sum_i U_{ii} a_i^2$ .

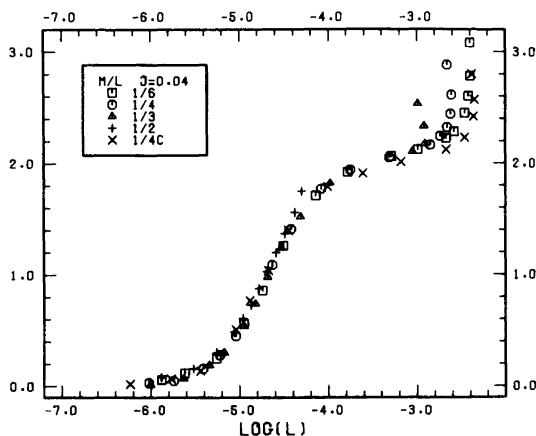


Fig. 1. Experimental data for Ni(II) plotted as curves  $\bar{n}(\log l)$ . The points  $\bar{n} > 2$  are probably affected by precipitation as in higher ionic strengths.

may indeed be disordered. Examination of Fourier maps throughout the course of the analysis did not reveal any meaningful disorder model, however. The best description of these atoms appears to be that of roughly tetrahedral groups undergoing considerable libration.

The atomic coordinates and isotropic temperature factors with standard deviations are given in Table 2. Lists of structure factors and anisotropic

thermal parameters are obtainable on request from the authors.

## RESULTS AND DISCUSSION

Fig. 1 illustrates the Bjerrum plot and Table 3 shows the  $\log \beta$  values obtained with statistical observations at the ionic strength of 0.04. In the higher ionic strengths, precipitation began when the pH reached the value of about 8.5. Final results for all systems are therefore evaluated with  $\bar{n} < 2$  and only  $\text{NiL}^{2+}$  and  $\text{NiL}_2^{2+}$  are included.

The formation curves are steep (Fig. 1), compared with the ethylenediamine nickel(II) system, for example, and it is difficult to determine the stability constant of  $\text{NiL}^{2+}$  with the same level of reproducibility and accuracy as for most diamines. Fig. 2 shows the distribution curves of the species calculated on the basis of the  $\log \beta$  values in Table 4.

The nickel(II) complex formation of *N*<sup>1</sup>-cyclohexyl-2-methyl-1,2-propanediamine described by Tomlinson *et al.*<sup>17</sup> seems to be very similar to that of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine. The authors report values  $\log \beta_{011} = 4.5$  and  $\log \beta_{012} = 9.8$  or  $\log \beta_{011} \sim 0$ ,  $\log \beta_{012} = 9.6$  and  $\log \beta_{013} = 13.5$  at 20 °C and 0.1 M KCl. The negative  $\log K_D$  values (Table 4) for the disproportionation reaction

Table 3. The calculated  $\log \beta_{pqr}$  values in the ionic strength 0.04 and at 25 °C, when different  $\bar{n}$  ranges have been used.

Number of points	$\bar{n}$ range	$-\log h$ range	$\beta_{011}$	$\beta_{012}$	$\chi^2$	<i>R</i>
105	0.01–1.95	5.2–8.8	4.51(1)	9.354(5)	67	0.0021
67	0.1–1.95	6.5–8.8	4.52(1)	9.351(4)	11	0.0022

Table 4. Overall ( $\beta_{pqr}$ ), stepwise ( $k_n$ ) and disproportionation ( $K_D$ ) constants for Ni(II) complexes of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine at 25 °C.

<i>I</i>	$\log \beta_{011}$	$\log \beta_{012}$	$\log k_2$	$\log K_D$
0.040	4.52(1)	9.351(4)	4.83(1)	–0.30(2)
0.051	4.61(1)	9.428(4)	4.82(1)	–0.21(2)
0.088	4.55(1)	9.419(5)	4.87(2)	–0.32(2)
0.533	4.67(1)	9.828(5)	5.16(2)	–0.49(3)
1.034	5.13(1)	10.367(5)	5.24(2)	–0.11(3)
2.030	5.53(2)	11.23(1)	5.70(3)	–0.17(5)

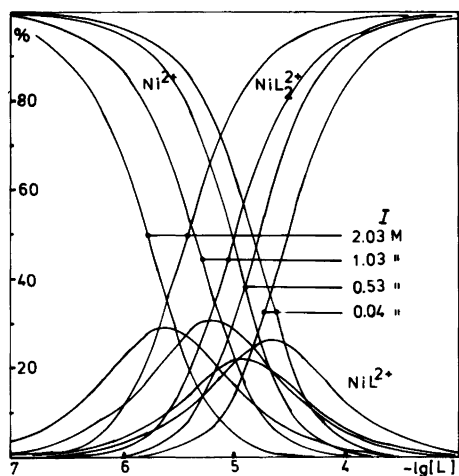
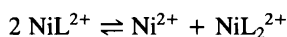


Fig. 2. The percentage distribution of various nickel(II) species as function of  $-\log I$  at 25 °C.



of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine suggest a change in the coordination geometry when  $\text{NiL}_2^{2+}$  is formed and more favoured formation of  $\text{NiL}_2^{2+}$  than  $\text{NiL}^{2+}$ , as found also for some *C*-alkyl substituted ethylenediamines.<sup>3-6</sup> The spectrochemical studies support these conclusions. The absorption maximum at 450 nm, which is typical for square-planar nickel(II) complexes, becomes with base addition predominant over the octahedral maximum at 400 nm even in solutions where total metal and ligand concentrations are equal (Fig. 3).

The stabilities of Ni(II) complexes of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine increases with increasing ionic strength more than those of octahedral Ni(II) diamine complexes. When ionic strength increases from 0.04 to 2.03 the changes in  $\log \beta_{011}$  and  $\log \beta_{012}$  are 1.0 and

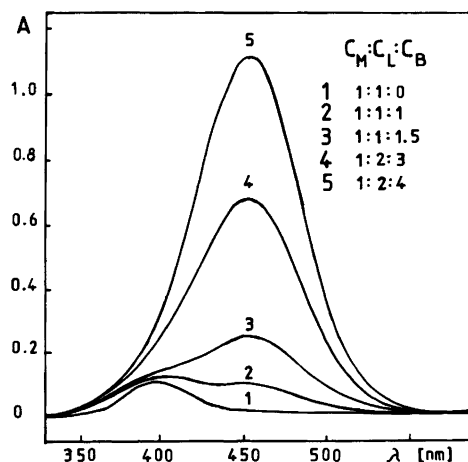


Fig. 3. Absorption spectra of Ni(II) complexes of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine in different conditions at  $I=0.14$ .

1.9 log units for the studied complexes and 0.6 and 1.2 log units for the ethylenediamine Ni(II) complexes, respectively.<sup>18</sup>

The yellow nickel(II) compound precipitated from titrated solutions is composed of  $[\text{NiL}_2]^{2+}$  complex cations and perchlorate ions loosely held together by hydrogen bonds and electrostatic forces (Fig. 4). The two crystallographically independent complexes exhibit a square-planar coordination geometry as shown in Fig. 5. Table 5 lists the bond lengths and angles characteristic of these species, while Table 6 summarizes the intermolecular distances below 3.4 Å.

The two nickel(II) complexes that form a part of the asymmetric unit are essentially the same. The four Ni-N distances of 1.900(7)–1.959(7) Å (av. 1.927 Å) in each complex are comparable to

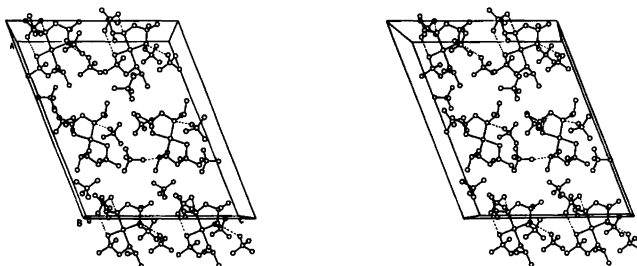


Fig. 4. A stereoview of the packing. Intermolecular distances below 3.1 Å are shown by dotted lines.

Table 5. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

Unit	A		B		A	B	A	B
	A	B	A	B				
Ni-N11	1.952(5)	1.959(7)	86.1(3)	85.4(3)	N21-Ni-N22	85.9(2)	85.6(3)	
Ni-N12	1.911(7)	1.900(7)	93.3(3)	93.6(3)	N21-Ni-N12	94.7(3)	95.3(3)	
Ni-N21	1.943(5)	1.930(7)	179.1(3)	178.8(3)	N22-Ni-N12	170.6(3)	171.7(3)	
Ni-N22	1.912(7)	1.912(7)						
C15-C17	1.479(10)	1.508(14)	112.3(8)	115.1(7)	C27-C25-C26	112.9(8)	111.2(7)	
C25-C27	1.491(11)	1.524(12)	111.8(7)	111.0(7)	C27-C25-N21	112.2(8)	111.1(6)	
C15-C16	1.475(12)	1.469(14)	112.7(6)	114.2(9)	C26-C25-N21	111.4(6)	112.8(8)	
C25-C26	1.506(14)	1.508(13)	113.9(6)	110.4(6)	C25-N21-C21	112.9(6)	111.6(6)	
C15-N11	1.519(10)	1.513(12)	115.5(4)	113.0(5)	C25-N21-Ni	116.5(5)	115.6(4)	
C25-N21	1.504(9)	1.493(12)	108.9(4)	109.8(6)	C21-N21-Ni	108.7(4)	110.4(6)	
N11-C11	1.487(12)	1.469(9)	109.7(6)	108.6(6)	N21-C21-C22	109.5(6)	109.6(6)	
N21-C21	1.492(11)	1.471(9)	111.8(6)	111.9(8)	C21-C22-C23	112.6(6)	112.9(8)	
C11-C12	1.498(11)	1.545(13)	113.0(7)	109.2(6)	C21-C22-C24	111.3(6)	108.2(7)	
C21-C22	1.509(9)	1.551(13)	103.6(6)	102.7(6)	C21-C22-N22	103.1(6)	101.6(6)	
C12-C13	1.546(12)	1.504(12)	108.9(7)	111.0(7)	C23-C22-C24	110.1(7)	112.0(6)	
C22-C23	1.519(12)	1.496(12)	108.5(6)	108.9(6)	C23-C22-N22	109.3(6)	109.4(6)	
C12-C14	1.513(14)	1.512(12)	110.9(6)	112.9(8)	C24-C22-N22	110.2(6)	112.3(7)	
C22-C24	1.536(13)	1.522(11)	106.8(4)	110.6(6)	C22-N22-Ni	110.0(4)	110.6(6)	
C12-N12	1.507(9)	1.477(11)						
C22-N22	1.476(10)	1.488(10)						
C11-O11	1.415(8)	1.383(12)	107.4(5)	113.5(7)	O21-C12-O22	106.8(6)	107.8(5)	
C11-O12	1.363(9)	1.321(8)	111.3(5)	115.1(7)	O21-C12-O23	107.9(5)	108.5(5)	
C11-O13	1.392(9)	1.397(11)	111.5(5)	95.5(8)	O21-C12-O24	109.2(4)	113.6(6)	
C11-O14	1.376(6)	1.344(14)	105.9(6)	113.6(6)	O22-C12-O23	111.3(5)	106.4(7)	
C12-O21	1.418(9)	1.401(6)	112.4(5)	113.8(8)	O22-C12-O24	111.3(4)	110.3(7)	
C12-O22	1.361(8)	1.387(10)	108.2(5)	103.5(8)	O23-C12-O24	110.2(4)	109.9(8)	
C12-O23	1.389(7)	1.361(11)						
C12-O24	1.421(6)	1.305(13)						

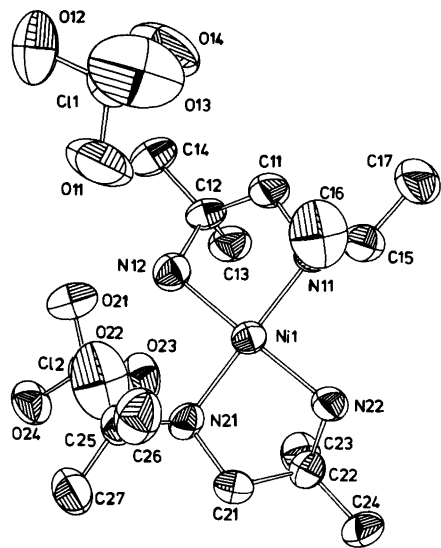


Fig. 5. A view of the A unit.

those found in square-planar nickel(II) complexes but considerably shorter than the Cu–N bond lengths of 1.973(4)–2.039(3) Å (av. 2.005 Å) in bis(*N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine)copper(II) malonate,<sup>19</sup> which is the only known square-planar copper(II) biscomplex of *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine. This difference in the metal–nitrogen bond lengths is equal to the difference in the ionic radii of Ni<sup>II</sup> and Cu<sup>II</sup> in square-planar complexes and a direct consequence of the removal of the unpaired electron from the  $d_{x^2-y^2}$  orbital of the  $d^9$  configuration of Cu<sup>II</sup> on going to the low-spin  $d^8$

nickel(II) complexes. The Ni–N(secondary) bonds are somewhat longer (~0.04 Å) than the Ni–N(primary) bonds, as is common for copper(II) complexes.<sup>20,21</sup>

At both nickel(II) centres the coordination plane has a slight tetrahedral distortion and the metal ions are situated 0.08 Å from the coordination plane on the side of the isopropyl substituents. The *N*-isopropyl and *C*-methyl substituents together prevent the formation of 5- or 6-coordinated complexes. The diamine chelate rings are in *gauche* conformation. In each chelate the dimethyl-substituted C atom (C12 or C22) is located *ca.* 0.65 Å below the N–Ni–N plane, while the other ring C atom (C11 or C21) lies *ca.* 0.05 Å above the same plane. A similar asymmetric chelate ring is found in *L*-lactatobis(*N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediamine)copper(II) and zinc(II) complexes<sup>22,23</sup> where in each case, however, one of the two chelate rings is much less asymmetric. Evidently the different intramolecular interactions and hydrogen bonding involving the amine nitrogen atoms cause this difference.

The perchlorate ions give evidence that their O atoms are undergoing marked thermal motion or have static disorder. It is clear from difference Fourier maps, however, that the observed disorder does not necessarily require the use of a number of fractionally weighted models for anions. Consequently, the calculated Cl–O bond lengths of 1.31(1)–1.42(1) Å, with an average of 1.38 Å, are shorter than normal.

The perchlorate ions are situated at hydrogen bond distances from complex cations (Table 6).

Table 6. Intermolecular contacts <3.4 Å.<sup>a</sup>

N11(A)···O12(A) <sup>ii</sup>	3.030(10)	N11(B)···O12(B)	3.135(13)
N12(A)···O11(A)	3.384(11)	N12(B)···O11(B) <sup>ii</sup>	3.342(14)
N12(A)···O22(A)	3.174(10)	N12(B)···O21(B) <sup>iii</sup>	3.042(10)
N12(A)···O24(A) <sup>i</sup>	3.277(8)	N12(B)···O14(B) <sup>ii</sup>	3.276(13)
N21(A)···O22(A)	2.867(10)	N21(B)···O22(B) <sup>iii</sup>	3.054(12)
N22(A)···O24(A) <sup>iv</sup>	3.222(9)	N21(B)···O21(B) <sup>iii</sup>	3.394(10)
N22(A)···O23(A) <sup>iv</sup>	3.055(9)	N22(B)···O23(B)	2.960(11)
N22(A)···O11(A) <sup>ii</sup>	3.279(9)	N22(B)···O11(B)	3.055(15)
N22(A)···O12(A) <sup>ii</sup>	3.211(9)	O21(A)···O22(A) <sup>i</sup>	3.263(10)
C25(A)···O22(A)	3.240(12)	C27(A)···O14(B)	3.367(14)
C26(A)···O23(A) <sup>iv</sup>	3.290(12)	C24(B)···O21(B) <sup>v</sup>	3.254(13)
C27(A)···O21(A) <sup>i</sup>	3.237(13)	C26(B)···O13(B) <sup>ii</sup>	3.307(13)

<sup>a</sup> Symmetry operations: i=1-x, -y, 1-z; ii=x, 1/2-y, z-1/2; iii=2-x, y-1/2, 1/2-z; iv=1-x, y+1/2, 1/2-z; v=2-x, 1-y, 1-z.

The perchlorate ions Cl2(A) and Cl2(B) connect the complex cations *A* and *B*, respectively, into chains parallel to the *b* axis. The other perchlorate ions, Cl1(A) and Cl1(B), have a space-filling role, connecting chains weakly together in the direction of the *c* axis. The intermolecular distances between so built *A* and *B* layers are greater than 3.36 Å.

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