

Structure and Redox Properties of Some Planar $[M^{II}N_4]$ Chelate Compounds ; of Cobalt and Nickel. ; Part IV. Crystal and Molecular Structure of 1,2-Bis(2-imino-benzylideneimino)- propanenickel(II)

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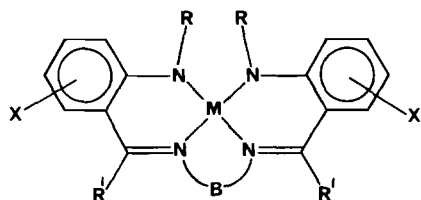
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Received May 22, 1980

Crystals of the title compound are orthorhombic with $a = 7.25(1)$, $b = 23.95(2)$, $c = 9.09(1)$ Å 1 space group $P2_12_12_1$ (No. 19). A three-dimensional X-ray analysis of the structure was made with 2172 reflections collected on a Stöe Stadi-2 automatic diffractometer. The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares to a final R of 0.059. The $[NiN_4]$ coordination polyhedron $\{Ni-N = 1.857(6)$, $1.878(9)$, $1.858(11)$, and $1.868(5)$ Å $\}$ is planar, with a small tetrahedral twist $\{\text{nitrogens } \pm 0.05$ Å and the Ni 0.003 Å out of the least-squares $[N_4]$ plane $\}$. It is significantly closer to planarity than the recently described isomorphous Cu compound. Evidence is given that the aliphatic central chelate ring is in two-fold disorder with axial methyls – the components of the disorder being the two optical isomers of the ligand. There is a marginal preference for one chiral form of the ligand in the chiral crystals.

Introduction

As part of our study [1–3] of the compounds I



$\{M = Co, Ni, Cu\}$, we have determined [1–3] the structure of $[Ni(abpn)]$ $\{I$ for $X = R = R' = H$; and $B = CH_2CH(CH_3)\}$.

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Since our first solution and refinement of the structure, using poor quality photographic data, Hall *et al.* have described [4] the structure of the isomorphous [1, 2] copper compound. Thus, in describing our results of the refinement with better quality data, we compare the Ni and Cu polyhedra, and give a different interpretation of the disorder that occurs in the aliphatic *pn* chelate ring.

Experimental

Red-brown prisms were obtained from acetone. The crystal used for the X-ray analysis had dimensions $0.28 \times 0.51 \times 0.69$ mm. *Crystal Data*: $C_{17}H_{17}N_4Ni$, $M = 336.1$, Orthorhombic, $a = 7.25(1)$, $b = 23.95(2)$, $c = 9.09(1)$ Å, $U = 1578.9$ Å 3 , $D_m = 1.40$ g cm $^{-3}$ (by flotation), $Z = 4$, $D_c = 1.41$ g cm $^{-3}$, $F(000) = 700$. Space group $P2_12_12_1$ (No. 19) from symmetry and systematic absences. $MoK\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(Mo-K\alpha) = 12.34$ cm $^{-1}$.

X-ray data with $6.5 < 2\theta < 50^\circ$ were collected from a crystal mounted up the c axis on a Stöe Stadi-2 automatic diffractometer, using graphite monochromated $MoK\alpha$ radiation.

Angular step-scan ranges were systematically varied to allow for variations in peak-width of the different reflections, and a counting time of 1.0 sec was used for each 0.01° increment of scan. Background counts were accumulated for 30 sec at each extremity of the scan.

Reflections with intensity $I < 3\sigma(I)$ were ignored, as were those with background difference $\Delta > 3\sigma$. Corrections were applied for Lorentz and polarisation factors and absorption. The (011) reflection was eventually removed because of probable extinction effects, and the final data set consisted of 2172 planes.

The structure was solved by conventional Patterson and Fourier techniques (initially using a poor quality set of $CuK\alpha$ photographic data [1]). Block

TABLE I. Atomic Positions and Thermal Vibrational Parameters, with Estimated Standard Deviations in Parentheses.

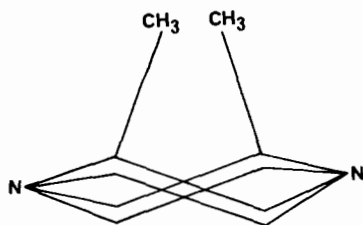
(a) Atomic positions ($\times 10^4$) and isotropic thermal parameters (\AA^2)						
Atom	x/a	y/b	z/c	B		
Ni	-1526.2(1.2)	-967.1(0.3)	-329.3(0.9)			
N(1)	-869(8)	-1413(2)	1258(6)			
N(2)	-3565(17)	-1418(3)	-788(9)	4.65		
N(3)	-2382(12)	-502(4)	-1816(14)	5.07		
N(4)	506(8)	-509(2)	39(6)			
C(1)	-1707(11)	-1860(3)	1818(7)			
C(2)	-1046(11)	-2120(3)	3131(8)			
C(3)	-1913(11)	-2580(3)	3742(9)			
C(4)	-3508(14)	-2813(3)	3032(9)			
C(5)	-4164(12)	-2582(3)	1766(10)			
C(6)	-3310(11)	-2099(3)	1143(8)			
C(7)	-4136(11)	-1868(3)	-135(9)			
C(8) ^a	-4387(14)	-1252(3)	-2242(9)	4.71		
C(9) ^a	-4441(18)	-611(3)	-2348(8)	5.07		
C(10) ^a	-3200(25)	-1486(5)	-3507(10)	6.46		
C(81) ^b	-5141(12)	-1113(4)	-1704(15)	5.07		
C(91) ^b	-3850(14)	-783(4)	-2723(9)	4.71		
C(101) ^b	-2946(26)	-1186(8)	-3832(13)	6.46		
C(11)	-1788(12)	-14(3)	-2238(10)			
C(12)	-185(10)	247(3)	-1667(8)			
C(13)	250(12)	784(3)	-2211(9)			
C(14)	1756(12)	1073(3)	-1706(9)			
C(15)	2930(11)	816(3)	-629(9)			
C(16)	2551(10)	281(3)	-94(8)			
C(17)	941(9)	-13(3)	-566(7)			
(b) Anisotropic thermal parameters ^c ($\times 10^4$)						
Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni	155.4(1.2)	15(0.1)	93.2(0.8)	2.3(0.7)	-55.8(2.4)	-5.5(0.9)
N(1)	188(12)	16(1)	119(8)	23(5)	-106(7)	-16(6)
N(4)	177(11)	16(1)	107(8)	11(4)	-80(16)	-22(6)
C(1)	208(16)	14(1)	95(7)	-5(5)	-33(21)	-1(8)
C(2)	247(19)	17(1)	118(9)	12(6)	-30(22)	-8(8)
C(3)	231(19)	19(1)	141(11)	8(7)	49(24)	-2(9)
C(4)	266(19)	19(1)	163(11)	10(7)	70(33)	-3(11)
C(5)	249(19)	18(1)	168(13)	1(7)	45(28)	-21(9)
C(6)	193(15)	16(1)	128(9)	-12(6)	0(23)	-18(8)
C(7)	253(18)	20(1)	147(12)	2(7)	-89(26)	-38(9)
C(11)	228(20)	23(2)	178(13)	43(8)	-129(29)	-21(11)
C(12)	156(13)	18(1)	117(9)	20(6)	4(19)	4(7)
C(13)	246(18)	18(1)	134(10)	18(6)	71(25)	10(8)
C(14)	231(18)	19(1)	158(11)	1(6)	149(26)	3(9)
C(15)	240(18)	20(1)	148(12)	-4(6)	64(24)	-23(8)
C(16)	200(15)	20(1)	124(11)	-2(6)	-1(21)	-25(8)
C(17)	159(12)	17(1)	99(8)	-1(5)	16(17)	6(6)

^aThese were refined, together with N(2), as a group of four atoms with idealised, fixed geometry. The refined population parameter for the three carbon atoms was 0.546. ^bThese were refined, together with N(3), as a fixed geometry group. The refined population parameter for the three carbon atoms was 0.454. ^cThe expression for the temperature factor is: $\exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + k l b_{23} + h l b_{13} + h k b_{12})]$.

diagonal least-squares refinement of the positional and isotropic thermal parameters of all non-hydrogen atoms led to unreal bondlengths and angles in the aliphatic *pn* chelate ring.

Accordingly, the three carbon atoms of this chelate ring were omitted, and a difference Fourier was obtained. This showed elongated peaks of electron-density which could readily be rationalised

assuming a two-fold disorder of the atoms of the *pn* chelate ring as shown in II.



The two $\text{CH}_2\text{CH}(\text{CH}_3)$ components of II have opposite chirality, so this model is consistent with the use of the racemic ligand in the preparations.

Hall *et al.* [4], in their analysis of the Cu isomorph, chose to interpret the disorder differently: allowing large thermal motions for a single three-atom component of the one chirality. Such spontaneous resolution has been known since Pasteur [5], but is rare, and we have now disproved it here by running circular dichroism spectra of an acetone solution obtained from a single crystal of the Ni compound. The optical activity was barely detectable and consistent with a small preference for one component of II (see below) but not with total spontaneous resolution.

For the further refinement then we calculated two idealised four-atom groups: {N(2), C(8), C(9), C(10)} and {C(81), C(91), C(101), N(3)}. The C–C distances were fixed at 1.54 Å and the C–N at 1.50 Å. All atoms of the calculated groups fitted within the observed electron-density.

Allowing anisotropic thermal parameters for the nickel, and allowing the relative populations of the three-atom groups to vary, whilst constraining the isotropic temperature parameters of related carbons to be equal, reduced R to 0.073. The refined populations of the carbon atoms of the disorder groups were, respectively, 0.56 and 0.44.

The use of (i) anisotropic thermal parameters for the non-hydrogen atoms, except those of the disorder groups; (ii) non-unit weights with $w_{hkl} = |F_{hkl}|/15$ for $|F_{hkl}| > 15$, otherwise $w = 1$; and (iii) anomalous dispersion corrections for all atoms (both $\Delta f'$ and $\Delta f''$) gave relative populations of 0.55 and 0.45 and a final R of 0.059.

Hydrogen atoms were not observed in final difference Fourier syntheses using either the full data set, or only the reflections with $\sin\theta/\lambda < 0.3$. Thus they were not included in the analysis. These difference Fouriers showed no features $> 10.2 \text{e}\text{\AA}^{-3}$ in the region of the disordered *pn* chelate ring, and none $> 10.5 \text{e}\text{\AA}^{-3}$ in the remainder of the unit cell.

The final atomic parameters are given in Table I.

Scattering factors and correction parameters were taken from International Tables for X-ray Crystallography (Vol. IV, 1974). Programmes used are part of the Sheffield X-ray system. Calculations were per-

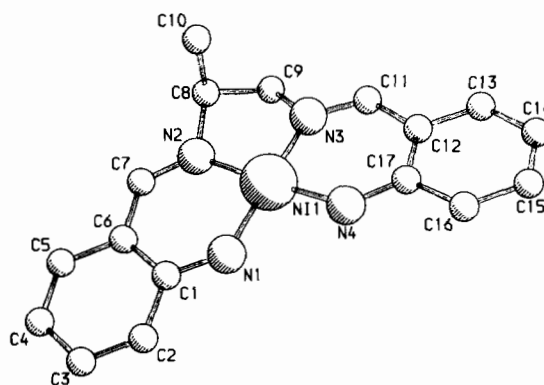


Fig. 1. The molecular geometry of 1,2-bis(2-imino-benzylideneimino)propanenickel(II) and atom labelling: the atoms of the disorder component of major occupancy are shown.

formed on the Sheffield University ICL 1907 computer. Observed and calculated structure factors are listed in a table available from the Editor.

Circular dichroism measurements were made on a CNRS-Roussel-Jouane Dichrographe III with an acetone solution ($\sim 10^{-4} \text{M}$) prepared from one crystal of [Ni(abpn)].

Results and Discussion

The molecular geometry is shown in Fig. 1, together with the atom labelling scheme. (The latter is the same as that of ref. 4).

Details of bond-lengths and angles are in Table II, and the relevant equations of least-squares planes and interplanar angles are listed in Table III.

The four Ni–N bond-lengths are identical within experimental error: mean = 1.865 Å. This compares with the different values [3] in [Ni(abtn)] {1 for X = R = R' = H; and B = $\text{CH}_2\text{CH}_2\text{CH}_2$ } of 1.860 for N(1)/N(4) and 1.923 for N(2)/N(3). We had previously suggested that these differences were a result of the different characters of nitrogens as anionic and neutral ligands. However, it now seems that they may owe more to the steric effects of different chelate ring size.

The M–N distances for [Ni(abpn)] are distinctly less than the 1.91 Å (av) observed for the isomorphous Cu compound [4], and the Ni compound is closer to planarity. [For the latter, compare the data of Table III here with that in Table V of ref. 4. For example, the angles between the *o*-iminobenzylideneimino planes are 13° for Ni and 15.2° for Cu, and the Ni compound has a marginally smaller tetrahedral twist than the Cu].

The methyl substituents are axial – probably constrained there by crystal-packing forces, although there is no reason to suspect significant steric

TABLE II. Interatomic Distances and Angles with Estimated Standard Deviations in Parentheses.

(a) Co-ordination Sphere of the Metal			
(i) Bond lengths (Å)			
Ni-N(1)	1.857(6)	Ni-N(3)	1.858(11)
Ni-N(2)	1.878(9)	Ni-N(4)	1.868(5)
(ii) Bond angles (°)			
N(1)-Ni-N(2)	92.5(3)	N(2)-Ni-N(3)	85.4(4)
N(1)-Ni-N(3)	174.5(4)	N(2)-Ni-N(4)	177.5(3)
N(1)-Ni-N(4)	89.8(2)	N(3)-Ni-N(4)	92.4(4)
(b) The Ligand			
(i) Bond lengths (Å)			
N(1)-C(1)	1.33(1)	N(4)-C(17)	1.34(1)
C(1)-C(2)	1.43(1)	C(17)-C(16)	1.43(1)
C(1)-C(6)	1.43(1)	C(17)-C(12)	1.43(1)
C(2)-C(3)	1.38(1)	C(16)-C(15)	1.40(1)
C(3)-C(4)	1.44(1)	C(15)-C(14)	1.44(1)
C(4)-C(5)	1.36(1)	C(14)-C(13)	1.37(1)
C(5)-C(6)	1.43(1)	C(13)-C(12)	1.41(1)
C(6)-C(7)	1.42(1)	C(12)-C(11)	1.42(1)
N(2)-C(7)	1.30(1)	N(3)-C(11)	1.30(1)
N(2)-C(81)	1.59(1)	N(3)-C(9)	1.59(1)
(ii) Bond angles (°)			
Ni-N(1)-C(1)	129.9(5)	Ni-N(4)-C(17)	129.0(5)
N(1)-C(1)-C(2)	121.1(6)	N(4)-C(17)-C(16)	120.2(6)
N(1)-C(1)-C(6)	121.9(6)	N(4)-C(17)-C(12)	122.4(6)
C(2)-C(1)-C(6)	117.0(6)	C(12)-C(17)-C(16)	117.4(6)
C(1)-C(2)-C(3)	122.0(7)	C(17)-C(16)-C(15)	120.5(7)
C(2)-C(3)-C(4)	119.6(7)	C(16)-C(15)-C(14)	120.9(7)
C(3)-C(4)-C(5)	120.2(8)	C(15)-C(14)-C(13)	118.9(7)
C(4)-C(5)-C(6)	120.8(8)	C(14)-C(13)-C(12)	121.3(7)
C(5)-C(6)-C(7)	117.2(7)	C(13)-C(12)-C(11)	120.9(6)
C(5)-C(6)-C(1)	120.4(7)	C(11)-C(12)-C(13)	117.1(7)
C(1)-C(6)-C(7)	122.4(7)	C(11)-C(12)-C(17)	122.1(7)
N(2)-C(7)-C(6)	124.3(8)	N(3)-C(11)-C(12)	123.9(8)
Ni-N(2)-C(7)	128.9(7)	Ni-N(3)-C(11)	129.9(8)
Ni-N(2)-C(8)	110.8(6)	Ni-N(3)-C(9)	115.9(7)
Ni-N(2)-C(81)	114.7(7)	Ni-N(3)-C(91)	111.6(7)
C(7)-N(2)-C(8)	119.7(8)	C(11)-N(3)-C(9)	111.6(9)
C(7)-N(2)-C(81)	113.1(8)	C(11)-N(3)-C(91)	118.2(9)

TABLE III. Equations to Some Least-squares Planes Given in the Form $lX + mY + nZ = d$ (where X , Y , and Z are coordinates in Å referred to the axes a , b , and c). Deviations (Å) of the various atoms from these planes are given in square brackets.

	l	m	n	d
Plane (1): N(1)-(4)	0.5563	-0.5354	-0.6355	-0.7837
	[Ni -0.031, N(1) 0.050, N(2) -0.051, N(3) 0.052, N(4) -0.050, C(1) 0.138, C(2) 0.297, C(3) 0.410, C(4) 0.344, C(5) 0.172, C(6) 0.088, C(7) -0.021, C(8) -0.346, C(9) 0.435, C(10) -1.857, C(11) 0.195, C(12) 0.212, C(13) 0.411, C(14) 0.465, C(15) 0.284, C(16) 0.061, C(17) 0.060, C(81) 0.446, C(91) -0.240, C(101) -1.763]			

(continued on facing page)

TABLE III. (continued)

	<i>l</i>	<i>m</i>	<i>n</i>	<i>d</i>
Plane (2): Ni, N(1), N(2) [C(1) -0.061, C(4) -0.207], C(6) -0.043, C(7) 0.004]	-0.5750	0.5554	0.6007	0.8295
Plane (3): Ni, N(3), N(4) [C(11) -0.114, C(12) -0.160, C(14) -0.400, C(17) -0.073]	-0.5356	0.5144	0.6697	0.7991
Plane (4): N(1), C(1)-(7), N(2) [N(1) 0.026, N(2) -0.054, C(1) 0.018, C(2) -0.009, C(3) -0.036, C(4) -0.013, C(5) 0.033, C(6) 0.027, C(7) 0.008, Ni -0.068, C(14) -0.865]	-0.5798	0.5896	0.5624	0.9602
Plane (5): N(3), C(11)-(17), N(4) [N(3) -0.003, N(4) 0.049, C(11) -0.015, C(12) -0.015, C(13) 0.007, C(14) 0.031, C(15) 0.002, C(16) -0.045, C(17) -0.012, Ni 0.150, C(4) 1.242]	0.5500	-0.4276	-0.7174	-0.7458
Plane (6): C(1)-(6) [C(1) 0.000, C(2) -0.007, C(3) 0.006, C(4) 0.003, C(5) -0.011, C(6) 0.009, C(7) 0.063, Ni 0.141, N(1) 0.005, N(2) 0.141, N(3) 0.440, N(4) 0.111]	0.5898	-0.5981	-0.5427	-1.0358
Plane (7): C(12)-(17) [C(12) 0.006, C(13) 0.010, C(14) -0.011, C(15) -0.004, C(16) 0.019, Ni -0.217, N(1) -0.567, N(2) -0.279, N(3) -0.031, N(4) -0.105, C(17) -0.019]	-0.5481	0.4115	0.7282	0.7809
Plane (8): Ni, N(2), N(3) [C(8) -0.351, C(9) 0.373, C(10) -1.874, C(81) 0.443, C(91) -0.297, C(101) -1.814]	0.5532	-0.5003	-0.6661	-0.7457
Angles between planes (°)				
	(2)-(3)	5.1	(1)-(6)	6.7
	(4)-(5)	167.0	(1)-(7)	171.1
	(1)-(4)	174.6	(2)-(4)	3.0
	(1)-(5)	7.8	(3)-(5)	174.3
	(6)-(7)	164.7		

problems for this conformation in such a four-coplanar molecule.

The model used for the disorder, to which we were led by our first observation of the difference Fourier map, appears to be largely confirmed by a circular dichroism experiment. This showed that a solution prepared from a single crystal of the compound had a barely detectable optical activity, which was consistent with a partial, but far from complete, resolution of optical isomers in the crystal. That is, it was consistent with our refined model of non-equal populations of the disorder groups. However, because of the artificial constraints imposed in the refinement, we place qualitative rather than quantitative significance on the refined population parameters.

Since the molecule's oblique-puckered (umbrella) shape is not perfectly symmetrical {cf. planes (4) and (5) in Table III} the two optical isomers of the compound will experience different strains in the chiral crystals. Thus it is not surprising that a small partial resolution should occur. [The strain comes [4] from associating a *gauche* conformation of the central aliphatic chelate ring with an oblique rather than a parallel-puckered [6] conformation of the whole molecule].

In our 1974 discussion [3] of the structure of [Ni(abtn)], we presented our view that the observed conformation in these species is probably imposed by crystal-packing constraints. We have little further to add in maintaining this view other than to note

a recent paper [7] on the spectra of [Co(abpn)]. A marked difference was found between water and non-aqueous solvents. We think this may reflect the adoption of different conformations in the different media.

Acknowledgements

We are indebted to the S.R.C. for financial support and to Dr. C. J. Hawkins for the circular dichroism spectra.

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