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Dimerization of Nickel(II) with a Tridentate α -Amine Oxime Ligand. A Crystal Structure Determination

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Received March 8, 1974

AIC40163A

The crystal structure of *N*-(6-amino-4-aza-3,3,6-trimethyl-2-heptylidenyl)hydroxanatonickel(II) ion as $[\text{Ni}_2(\text{BnAO-H})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ has been determined utilizing scintillation counter techniques in a three-dimensional X-ray diffraction study. The diamagnetic compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 9.573$ (4) Å, $b = 11.359$ (4) Å, $c = 7.667$ (3) Å, $\alpha = 99.50$ (2)°, $\beta = 112.89$ (2)°, and $\gamma = 96.84$ (2)°. The density of 1.457 (2) g/cm³ calculated on the basis of 1 dimer per unit cell agrees with the flotation density of 1.43 (1) g/cm³. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares treatment to a conventional R factor of 2.6% using 1992 independent reflections above 3σ . The complex ion is dimeric with two bridging oxime groups. Nickel coordination is nearly square planar with the parallel planes about each nickel slightly displaced from each other. Coordination around each nickel ion involves two amine nitrogens and an oxime nitrogen from one ligand and the oxime oxygen from the other ligand with Ni-N(amine) = 1.872 (2), 1.913 (2) Å, Ni-N(oxime) = 1.861 (2) Å, and Ni-O = 1.836 (2) Å. The intramolecular Ni-Ni distance is 3.631 (2) Å, judged to be too large for significant interaction. The chloride ions are not coordinated but are hydrogen bonded to the amine hydrogens and the waters of hydration. The solution proton nmr and magnetic characteristics are consistent with the solid structure.

Introduction

The reaction of 2-methyl-1,2-diaminopropane with 2 equiv of 3-methyl-3-chloro-2-butanone oxime yielded a potentially tridentate ligand, BnAO (Figure 1), instead of the expected tetradentate molecule. It was not clear from electronic spectra and nmr measurements which end of the diamine reacted and thus which organic isomer was obtained (if not both). Reaction with $\text{Ni}(\text{aq})^{2+}$ produced a single complex with somewhat unusual properties which, based on nmr, electronic spectra, analysis, and magnetic measurements, could have had any of several structures. The orange complex ion had the empirical formula $\text{Ni}(\text{BnAO-H})\text{Cl} \cdot (2-3)\text{H}_2\text{O}$,¹ was diamagnetic, and showed no ir or nmr evidence of an intramolecular hydrogen bond. The unusual empirical formula and properties prompted a determination of the molecular structure through a single-crystal X-ray study. The complex ion will be shown to be a dimer, utilizing four ligand atoms for coordination and is of especial interest due to the opportunity it presents for study of the kinetics and thermodynamics of dimerization of a planar complex ion.

Experimental Section

Complex and Crystal Preparation. The ligand $\text{NH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{-NHC}(\text{CH}_3)_2\text{C}(\text{CH}_3)=\text{NOH}$ was prepared by refluxing for 8 hr a 1:1 or 1:2 mixture of 2-methyl-1,2-diaminopropane and 3-methyl-3-chloro-2-butanone oxime in absolute methanol. Isolation was accomplished by techniques similar to those used previously² on related compounds. The equivalent weight by acid titration of the free amine was 94.1 ± 0.3 ; that calculated for $\text{C}_9\text{H}_{21}\text{N}_3\text{O}$ is 93.6.

The complex ion was formed in aqueous solution by neutralizing a 1:1 molar solution of $\text{Ni}(\text{ClO}_4)_2(\text{aq})$ -ligand to a pH of 7 with NaOH solution. The orange product was crystallized from solution by the addition of excess $\text{NaClO}_4(\text{s})$. After crystallization from water the perchlorate salt was converted to the chloride salt by passing a solution of it through a large excess of an ion-exchange resin (Dowex 1-X4) in the chloride form. The eluent was evaporated to near dryness under vacuum and suitable crystals for structure determination were obtained by slow evaporation of the solvent water. *Anal.* Calcd for $[\text{Ni}_2(\text{BnAO-H})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$; $\text{Ni}_2\text{Cl}_2\text{O}_7\text{N}_6\text{C}_{18}\text{H}_{50}$: Ni, 18.04; C, 33.21; H, 7.74; N, 12.91; Cl, 10.89; O, 17.21. Found: Ni, 18.55;

(1) The designation -H represents the essentially complete ionization of the oxime hydrogen of the ligand to $\text{H}(\text{aq})^+$. From the analysis one could not discern the precise number of water molecules present. Based on one nickel the X-ray data show 2.5 waters of hydration.

(2) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967).

C, 34.16; H, 7.64; N, 13.28; Cl, 11.20, 10.98; O (by difference), 15.17.

Physical Measurements. Magnetic susceptibility measurements at 30° on the solid were carried out by the Gouy method utilizing $\text{HgCo}(\text{SCN})_4$ as a standard. Two field strengths were used and a diamagnetic correction of -168×10^{-6} and $n\alpha$ of $+60 \times 10^{-6}$ were utilized.

The nmr method³ of magnetic susceptibility measurement was used for solutions at 40° in water and DMSO. Calibration was accomplished with diamagnetic $[\text{Ni}(\text{AO})_2\text{-H}]\text{ClO}_4$ and paramagnetic $[\text{Cu}(\text{AO})_2\text{-H}]\text{ClO}_4$ solutions.

Proton nmr measurements were carried out on a Varian A-60 instrument at 30–40° utilizing tms as an internal standard.

Visible spectra were measured with a Cary Model 12 spectrometer at 25°.

X-Ray Data Collection. Preliminary precession photographs indicated a triclinic cell ($P\bar{1}$ or $P\bar{1}$) with dimensions $a = 12.99$ (2) Å, $b = 9.60$ (1) Å, $c = 7.65$ (1) Å, $\alpha = 112.9$ (2)°, $\beta = 99.1$ (2)°, and $\gamma = 114.1$ (2)°.

A crystal bounded by 10 faces with maximum dimension of about 0.35 mm and minimum dimension of about 0.15 mm was mounted along the reciprocal c axis for the intensity data collection. The crystal was centered on a Picker four-angle diffractometer, and the setting angles of 29 reflections in the 20–35° 2θ region were determined using $\text{Mo K}\alpha_1$ at a low takeoff angle with a narrow vertical aperture at the counter. These setting angles were used for a least-squares refinement of the cell parameters.⁴ These refined parameters were subjected to a Delaunay reduction which yielded reduced cell parameters of $a = 9.573$ (4) Å, $b = 11.359$ (4) Å, $c = 7.667$ (3) Å, $\alpha = 99.50$ (2)°, $\beta = 112.89$ (2)°, and $\gamma = 96.84$ (2)°. These cell parameters were used in all subsequent work. The density calculated for one dimer in the unit cell is 1.457 (2) g/cm³ compared with a density of 1.43 (1) g/cm³ determined by flotation in $\text{CH}_2\text{Cl}_2\text{-CHCl}_3$.

The refinement using the 29 centered reflections was used to calculate the setting angles for all reflection measured. The intensities of 3642 reflections were measured out to a 2θ angle of 50°. The count rate never exceeded 8000 counts/sec and was thus in the linear region of the scintillation counter. The diffracted $\text{Mo K}\alpha$ radiation was filtered through 1 mil of niobium foil in front of a 3 mm \times 3 mm aperture at a takeoff angle of 2.0°. A scan rate of 1.0°/min was used for the variable nonsymmetric 2θ scan which was taken

(3) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(4) All calculations were performed on the IBM 360/65 computer of the University of Missouri—Columbia Computer Research Center using the following programs: S. L. Lawton, TRACERA, Delaunay reduction program; W. C. Hamilton, SORTH, sorting program; W. C. Hamilton and J. A. Ibers, NUPIK, Picker input program; W. C. Hamilton, NUCLS, least-squares program; a modification of W. Busing and H. Levy's program; A. Zalkin, FORDAP, Fourier program; W. Busing and H. Levy, ORFFE, function and error program; C. Johnson, ORTEP, thermal ellipsoid plot program; local data processing programs; W. C. Hamilton, HORSE, general absorption program, a modification of GONO9.

Table I. Atomic Positional and Anisotropic Thermal Parameters^a

Atom	x	y	z
Ni	-0.01780 (3)	-0.11790 (3)	-0.20301 (4)
Cl(1)(O(4)) ^b	0.3377 (2)	0.0208 (2)	-0.4132 (2)
Cl(2)	1/2	1/2	0
O(1)	-0.1590 (2)	0.0121 (2)	0.0223 (2)
O(2)	0.2292 (3)	-0.3507 (2)	-0.0780 (3)
O(3)	0.3371 (3)	-0.1343 (2)	0.2345 (4)
N(1)	-0.1635 (2)	-0.0895 (2)	-0.1046 (3)
N(2)	-0.1845 (2)	-0.2341 (2)	-0.3974 (3)
N(3)	0.1061 (2)	-0.1772 (2)	-0.3290 (3)
C(1)	-0.2855 (3)	-0.1737 (2)	-0.1673 (3)
C(2)	-0.2920 (3)	-0.2825 (2)	-0.3137 (3)
C(3)	-0.1279 (3)	-0.3240 (2)	-0.5035 (4)
C(4)	0.0067 (3)	-0.2563 (2)	-0.5275 (3)
C(5)	-0.4150 (3)	-0.1678 (3)	-0.0984 (4)
C(6)	-0.4546 (3)	-0.3296 (3)	-0.4751 (4)
C(7)	-0.2332 (3)	-0.3813 (2)	-0.2090 (4)
C(8)	-0.0451 (3)	-0.1745 (3)	-0.6688 (4)
C(9)	0.0940 (3)	-0.3447 (3)	-0.5915 (4)

	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Ni	0.00546 (5)	0.00281 (4)	0.00894 (8)	0.00047 (3)	0.00261 (4)	0.00036 (4)
Cl(1)	0.0120 (2)	0.0076 (2)	0.0197 (4)	0.0021 (2)	0.0072 (2)	0.0046 (2)
Cl(2)	0.0181 (2)	0.0087 (1)	0.0324 (3)	0.0036 (1)	0.0166 (2)	0.0048 (2)
O(1)	0.0063 (2)	0.0038 (2)	0.0132 (4)	0.0006 (2)	0.0032 (2)	-0.0020 (2)
O(2)	0.0221 (4)	0.0108 (3)	0.0263 (3)	0.0071 (3)	0.0048 (4)	0.0043 (3)
O(3)	0.0299 (6)	0.0098 (3)	0.0281 (7)	0.0089 (3)	-0.0012 (5)	0.0029 (4)
N(1)	0.0063 (3)	0.0030 (2)	0.0094 (4)	0.0007 (2)	0.0025 (3)	0.0004 (3)
N(2)	0.0067 (3)	0.0031 (2)	0.0111 (4)	0.0002 (2)	0.0032 (3)	0.0004 (2)
N(3)	0.0075 (3)	0.0035 (2)	0.0126 (5)	0.0009 (2)	0.0041 (3)	0.0009 (3)
C(1)	0.0064 (3)	0.0035 (3)	0.0102 (5)	-0.0007 (2)	0.0027 (3)	0.0012 (3)
C(2)	0.0069 (3)	0.0030 (3)	0.0123 (6)	-0.0002 (2)	0.0038 (3)	0.0005 (3)
C(3)	0.0100 (4)	0.0032 (3)	0.0144 (6)	0.0002 (2)	0.0057 (4)	-0.0014 (3)
C(4)	0.0084 (3)	0.0036 (3)	0.0106 (5)	0.0011 (2)	0.0037 (3)	-0.0003 (3)
C(5)	0.0083 (4)	0.0059 (3)	0.0192 (7)	0.0001 (2)	0.0069 (4)	0.0006 (4)
C(6)	0.0080 (4)	0.0051 (3)	0.0176 (7)	0.0013 (3)	0.0038 (4)	0.0013 (4)
C(7)	0.0119 (4)	0.0039 (3)	0.0181 (7)	0.0012 (3)	0.0074 (4)	0.0025 (3)
C(8)	0.0108 (4)	0.0073 (3)	0.0131 (6)	0.0021 (3)	0.0051 (4)	0.0033 (4)
C(9)	0.136 (4)	0.0054 (3)	0.0185 (7)	0.0026 (3)	0.0088 (5)	0.0001 (4)

^a The standard deviations from the least-squares refinement are given in parentheses in this and subsequent tables. ^b This position is occupied half by Cl and half by H₂O.

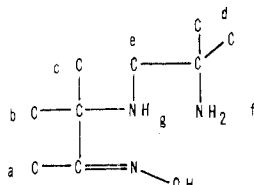


Figure 1. Structure of BnAO.

from 0.45° below the 2 θ setting for $K\alpha_1$ (λ 0.70926 Å) to 0.47° above the setting for $K\alpha_2$ (λ 0.71354 Å). Stationary background counts of 20 sec were taken at both the high and low-angle ends of the scan. Three reflections chosen as standards were measured after every 50 reflections to check for short-range changes in intensity while a set of 20 standard reflections was measured approximately every 20 hr during data collection to obtain an accurate long-range fluctuation measurement. Because of electronic problems with the instrument, correction factors as large as 6% had to be applied to some of the data in order to place the data on a common scale.

X-Ray Data Reduction. Corrections for background and Lorentz-polarization effects and the counting statistics standard deviations were calculated using formulas previously described.⁵ The dimensions of the crystal and the indices of the 10 faces were determined by optical goniometric and microscope techniques. All reflection intensities were corrected for absorption (μ 15.0 cm⁻¹). The transmission correction factor ranged from 0.78 to 0.86.

Of the 3642 measured reflections, 2010 reflections were independent assuming space group $P\bar{1}$, and 1304 of these were measured more than once, either as duplicates or as equivalent forms. The agreement of Friedel pairs seemed to justify the choice of space group $P\bar{1}$. Of these independent reflections 1992 had $F_o^2 > 3\sigma$

(5) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(F_o^2) where $\sigma(F_o^2) = [\sigma_{\text{counting}}^2 + (0.03F_o^2)^2]^{1/2}$. These reflections were used for the structure solution and refinement.

Determination and Refinement of the Structure. From a three-dimensional Patterson synthesis the nickel atom was located. From a Fourier synthesis using phasing from the nickel position, the chlorine atoms and the majority of the oxygen, nitrogen, and carbon atoms were located. After some refinement of these atom positions, a difference Fourier synthesis revealed the remaining nonhydrogen atoms. Additional least-squares refinement was followed by another difference Fourier synthesis which revealed the location of most of the hydrogen atoms. The remainder of the hydrogen atoms were placed in chemically reasonable positions.

In all calculations, the scattering factors used for Ni and Cl were those of Cromer and Waber,^{6a} while the anomalous scattering for these atoms was taken from Cromer^{6b} and included in F_c in the refinements.⁷ Scattering factors for the remaining atoms were taken from Ibers.⁸ Least-squares refinements of the nonhydrogen atoms in fixed positions from above, minimizing the function $\sum w \cdot (|F_o|^2 - |kF_c|^2)^2$, converged with $R_1 = \sum (|F_o|^2 - |kF_c|^2) / \sum |F_o|^2 = 0.048$ and $R_2 = [\sum w (|F_o|^2 - |kF_c|^2) / \sum w |F_o|^4]^{1/2} = 0.098$. In the above functions the weight $w = 1/\sigma^2$. Allowing the positional parameters of the hydrogen atoms to vary with fixed isotropic temperature factors ($B = 5-7 \text{ \AA}^2$) chosen according to the vibrational parameters of the atom to which each hydrogen was attached reduced R_1 to 0.039 and R_2 to 0.070. The conventional agreement factor ($R = \sum |F_o| - |F_c| / \sum |F_o|$) was 0.026. The standard deviation of an observation of unit weight was 1.72. A final difference Fourier synthesis was carried out as a check on the correctness of the structure. The

(6) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965); (b) D. T. Cromer, *ibid.*, 17 (1965).

(7) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(8) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.31A.

highest residual peak was $0.3 \text{ e}/\text{\AA}^3$. Because of the half-occupancy found for Cl(1) and H_2O , the possibility exists that there is a slight deviation from the centrosymmetric space group. However, the success of the refinement in $P\bar{1}$ indicates that refinement in $P1$ is not justified.

The observed and calculated structure factors ($\times 10$) appear only in the microfilm edition of the journal.⁹ The final positional and thermal parameters of the nonhydrogen atoms are given in Table I.

Results and Discussion

The pH titration of a 1:1 (in equivalents) metal:ligand- $(\text{H})_2^{2+}$ solution (10^{-2} M) with OH^- showed the complex to form reversibly over the pH range 4–7. The rate of reaching equilibrium was slow, characteristic of many planar Ni(II) complexes. Three equivalents of OH^- was used to complete the formation, but the gradual nature of the pH curve prevented precise end point evaluation.

The visible absorption spectra show a sharp absorption at 454 nm (water) and 457 nm (DMSO) with molar absorptivities of 224 and 278, respectively. The absorbance in water rose to 280 in the presence of a 2-equiv excess of ligand suggesting some dissociation in water. Very strong absorption occurs below 350 nm. The ir spectra show no evidence of the $-\text{OHO}-$ bond at 1580 cm^{-1} as seen in related amine oxime and dioxime ligand complexes with Ni(II).

The proton nmr were sharp, suggesting diamagnetism of the metal ion in the complex. For the ligand, four CH and, for the complex, five CH absorptions were observed as shown in Table II. No oxime hydrogen (10–15 ppm) or H-bonded dioxime (18 ppm) absorptions could be found. The assignments were made on the basis of similar monomeric complex ions.¹⁰

The solid magnetic susceptibility was $(+170 \pm 70) \times 10^{-6}$ per metal ion, essentially diamagnetic within the diamagnetic correction error. In solution the values 60 and 40×10^{-6} for DMSO and water solutions, respectively, were obtained for the molar susceptibility of the complex ion.

The above measurements show the ligand to have the structure given in Figure 1. It forms a diamagnetic Ni(II) complex without the usual OHO bond where the b and c carbons are not equivalent. Several structures can fit these observations including the dimeric structure found. Little change in the complex appears to occur upon solution since the magnetic susceptibility is not altered significantly, and the visible spectra are essentially the same in H_2O and DMSO.

Nature of Structure. The structure consists of discrete binuclear nickel(II) complex positive ions, chloride ions, and waters of hydration. The binuclear complex has each nickel in nearly square-planar four-coordination. The two amine nitrogens and the oxime nitrogen of one amine oxime ligand are coordinated to one nickel while the oxime-oxygen bridges in coordination to the other nickel so that the two nickel atoms are held together by two oxime bridges (Figure 2). This produces a six-membered ring containing two nickels, two nitrogens, and two oxygens with a center of symmetry in the middle of the ring. The resulting complex has a 2+ charge which is balanced by two crystallographically independent chloride ions (Figure 3), one in a special position (inversion center) and the other occupying a general position with an occupancy factor of 0.5. There are five molecules of water per binuclear complex, one of which occupies the same general position as the chloride ion with an occupancy

Table II. Pmr of Ligand and Complex (ppm from TMS)^a

Ligand	Intens	Complex	Assignment	
			Intens	(Figure 1)
0.96	6	1.06	6	d
1.12	6	1.39	3	c
		1.56	3	b
1.72	3	1.88	3	a
2.04	2	2.30	2	e
4.57 ^b	2	4.69 ^b	2	f
		5.72 ^b	1	g

^a In DMSO- d_6 at 35° . ^b Broad.

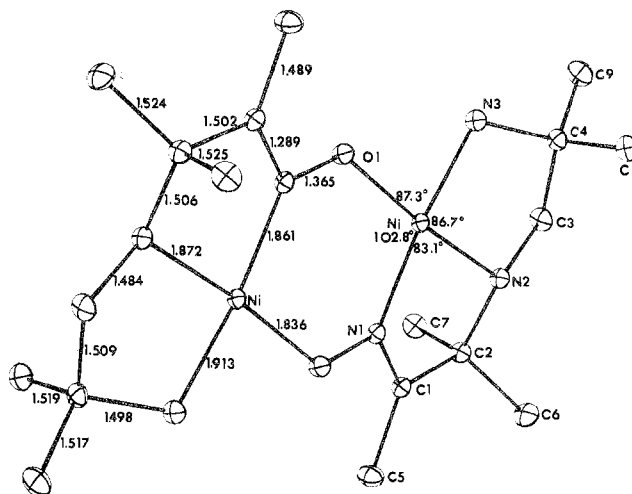


Figure 2. Bond distances in the $[\text{Ni}_2(\text{BnAO-H})_2]^{2+}$ ion.

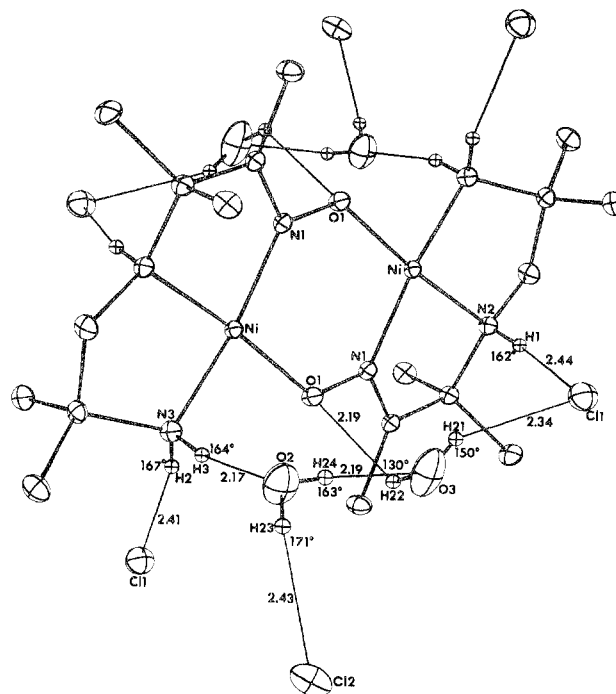


Figure 3. Hydrogen bonds among the nickel complex, the chloride ions, and the waters of hydration.

factor of 0.5. A nearly equivalent agreement was obtained by refining the structure with only chloride ion in that position and varying the occupancy factor. The occupancy factor converged to 0.737 (3) which is a reasonable value for half-occupancy by chloride and half-occupancy by water.

In Figure 3 the hydrogen bonding among chloride ions, waters, and amine groups in the complex ion is shown. This hydrogen bonding plays a major role in determining the crys-

(9) See paragraph at end of paper regarding supplementary material.

(10) See ref 1 and Ph.D. thesis of E. G. Vassian, University of Missouri, Columbia, Mo., 1967.

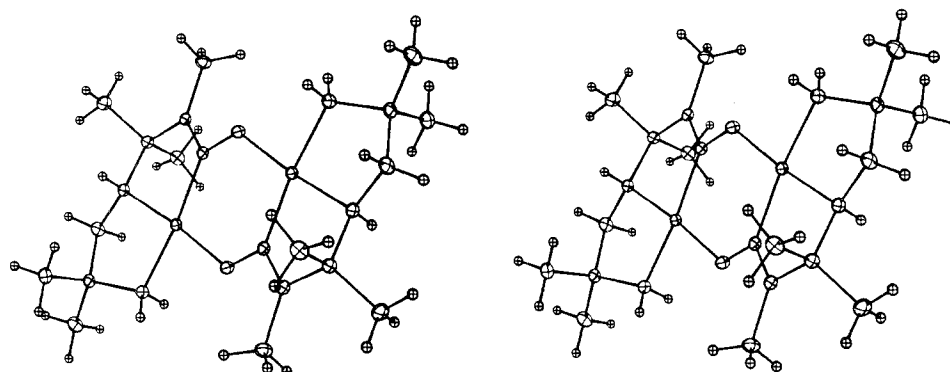


Figure 4. Stereoscopic view of the nickel complex showing the hydrogen atom positions. Orientation identical with that of Figure 2.

Table III. Hydrogen Atom Positional Parameters

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	-0.236 (4)	-0.192 (3)	-0.468 (5)
H(2)	0.174 (4)	-0.116 (4)	-0.331 (5)
H(3)	0.159 (4)	-0.219 (4)	-0.254 (5)
H(4)	-0.088 (4)	-0.381 (3)	-0.422 (5)
H(5)	-0.204 (4)	-0.369 (4)	0.383 (6)
H(6)	-0.451 (4)	-0.388 (4)	0.426 (6)
H(7)	0.481 (4)	-0.365 (4)	-0.423 (6)
H(8)	-0.493 (5)	-0.266 (4)	0.468 (6)
H(9)	-0.123 (5)	-0.352 (4)	-0.123 (6)
H(10)	-0.288 (5)	-0.395 (4)	-0.129 (6)
H(11)	-0.250 (4)	-0.457 (4)	-0.294 (6)
H(12)	-0.112 (5)	-0.221 (4)	0.217 (6)
H(13)	0.042 (5)	-0.134 (4)	0.316 (6)
H(14)	-0.097 (4)	-0.111 (4)	0.375 (6)
H(15)	0.028 (4)	-0.403 (4)	0.290 (6)
H(16)	0.179 (5)	-0.299 (4)	0.390 (6)
H(17)	0.131 (5)	-0.389 (4)	0.492 (6)
H(18)	-0.376 (4)	-0.111 (4)	0.036 (6)
H(19)	-0.458 (4)	-0.249 (4)	-0.108 (6)
H(20)	-0.486 (5)	-0.131 (4)	-0.177 (6)
H(21)	0.306 (6)	-0.107 (5)	0.295 (7)
H(22)	0.340 (5)	-0.095 (4)	0.163 (7)
H(23)	0.287 (5)	-0.392 (4)	-0.069 (7)
H(24)	0.254 (5)	-0.306 (4)	0.012 (7)

tal packing. The Cl(1) atom positions are those that are occupied in 50% of the crystal by water molecules. The distances and angles shown in Figure 3 are those for hydrogen bonds. The distances are not highly accurate because of the approximate nature of the hydrogen atom positions (Table III). The bond distances and angles associated with the hydrogen atoms are given in Table IV. In Figure 4 the positions of the hydrogen atoms can be seen. Since the shortest intermolecular or interionic contacts are not significantly different from expected van der Waals distances, only the hydrogen-bond distances are given in Table V.

The degree of planarity in the structure can be seen from Table VI which presents the least-squares coordination plane and the distances of the atoms in the dimer from this plane. This can also be seen from the stereoscopic view (Figure 4). The coordination around each nickel is nearly square planar. N(1) and N(3) deviate the most from the least-squares plane (~ 0.07 Å). The coordination planes about the two nickel atoms are displaced from each other by about 0.26 Å but are parallel. As in the bis(2-amino-2-methyl-3-butanone oximate)nickel(II) ion $[\text{Ni}(\text{AO})_2\text{-H}]^+$,¹¹ the trigonal carbon (C(1)) and the tetrahedral carbon (C(2)) of the amine oxime chelate ring are both on the same side of the nickel square plane, as are the attached methyl carbons (C(5)), C(6), and C(7)). The substituted ethylenediamine ring is in the usual

Table IV. Bond Distances^a and Angles Involving Hydrogen Atoms

Distances, Å			
N(2)-H(1)	0.83	C(7)-H(10)	0.97
N(3)-H(2)	0.90	C(7)-H(11)	0.95
N(3)-H(3)	0.86	C(8)-H(12)	0.89
C(3)-H(4)	0.98	C(8)-H(13)	0.96
C(3)-H(5)	0.91	C(8)-H(14)	1.01
C(5)-H(18)	1.03	C(9)-H(15)	0.96
C(5)-H(19)	0.95	C(9)-H(16)	0.99
C(5)-H(20)	0.93	C(9)-H(17)	0.88
C(6)-H(6)	0.95	O(3)-H(21)	0.70
C(6)-H(7)	0.94	O(3)-H(22)	0.77
C(6)-H(8)	0.93	O(2)-H(23)	0.76
C(7)-H(9)	0.98	O(2)-H(24)	0.73
Angles, Deg			
C(4)-C(8)-H(12)	108	Ni-N(2)-H(1)	103
C(4)-C(8)-H(13)	110	H(2)-N(3)-H(3)	107
C(4)-C(8)-H(14)	112	H(2)-N(3)-C(4)	113
H(12)-C(8)-H(13)	109	H(2)-N(3)-Ni	116
H(12)-C(8)-H(14)	109	H(3)-N(3)-C(4)	110
H(13)-C(8)-H(14)	109	H(3)-N(3)-Ni	104
C(4)-C(9)-H(15)	112	C(4)-C(3)-H(4)	107
C(4)-C(9)-H(16)	109	C(4)-C(3)-H(5)	114
C(4)-C(9)-H(17)	112	N(2)-C(3)-H(4)	108
H(15)-C(9)-H(16)	110	N(2)-C(3)-H(5)	113
H(16)-C(9)-H(17)	110	H(4)-C(3)-H(5)	107
H(17)-C(9)-H(15)	104	C(1)-C(5)-H(18)	114
H(23)-O(2)-H(24)	111	C(1)-C(5)-H(19)	109
H(21)-O(3)-H(22)	110	C(1)-C(5)-H(20)	110
H(7)-C(6)-H(8)	106	H(18)-C(5)-H(19)	113
C(2)-C(7)-H(9)	108	H(18)-C(5)-H(20)	102
C(2)-C(7)-H(10)	109	H(19)-C(5)-H(20)	109
C(2)-C(7)-H(11)	114	C(2)-C(6)-H(6)	109
H(9)-C(7)-H(10)	108	C(2)-C(6)-H(7)	110
H(9)-C(7)-H(11)	111	C(2)-C(6)-H(8)	110
H(10)-C(7)-H(11)	107	H(6)-C(6)-H(7)	112
C(2)-N(2)-H(1)	102	H(6)-C(6)-H(8)	110
C(3)-N(2)-H(1)	112		

^a The estimated error in the bond distances is approximately 0.1 Å based on the standard deviations from Table III.

Table V. Hydrogen Bond Distances Å^a

Cl(1)-N(2)	3.286	Cl(2)-O(2)	3.183
Cl(1)-N(3)	3.286	N(3)-O(2)	3.003
Cl(1)-O(3)	2.968	O(1)-O(3)	2.750
Cl(1)-O(3)	2.894	O(2)-O(3)	2.894

^a Hydrogen atoms are not included.

configuration with C(3) and C(4) on opposite sides of the plane.

In Table VII⁹ are the rms displacements of the ellipsoids of vibration. The nickel is nearly isotropic but has its maximum vibration nearly perpendicular to the square plane. The ellipsoid orientations for the remainder of the atoms are in general reasonable (see Figure 4).

Bond Distances and Angles. The bond distances and angles are given in Table VIII. As observed in the bis(2-amino-

(11) E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, **54**, 3990 (1971).

Table VI. Ni, N(1), N(2), N(3), O(1) Least-Squares Plane^a
[0.91 (2) X - 9.5 (2) Y + 4.83 (8) Z - 0.129 (3) = 0]

Atom	Dist from plane, Å	Atom	Dist from plane, Å
Ni	-0.0030 (3)	C(1)	0.458
N(1)	0.069 (2)	C(2)	0.779
N(2)	0.013 (2)	C(3)	0.409
N(3)	0.066 (2)	C(4)	-0.242
O(1)	0.023 (2)	C(5)	0.619
O(1) ^b	-0.281	C(6)	0.300
N(1) ^b	-0.327	C(7)	2.279
N(2) ^b	-0.266	C(8)	-1.737
N(3) ^b	-0.323	C(9)	0.383
Ni ^b	-0.253		

^a The weights used to derive the plane were those obtained from the least refinement of the atom positions. ^b These atoms are in the other half of the dimer related by a center of symmetry.

Table VIII. Intramolecular Distances and Angles

Distances, Å			
Ni-N(1)	1.861 (2)	C(2)-C(6)	1.525 (3)
Ni-N(2)	1.872 (2)	C(2)-C(7)	1.524 (3)
Ni-N(3)	1.913 (2)	N(2)-C(3)	1.484 (3)
Ni-O(1)	1.836 (2)	C(3)-C(4)	1.509 (3)
N(1)-O(1)	1.365 (3)	C(4)-N(3)	1.498 (3)
N(1)-C(1)	1.289 (3)	C(4)-C(8)	1.519 (4)
C(1)-C(2)	1.502 (4)	C(4)-C(9)	1.517 (3)
C(1)-C(5)	1.489 (3)	Ni-Ni	3.631 (2)
C(2)-N(2)	1.506 (3)		
Angles, Deg			
C(3)-C(4)-N(3)	104.1 (2)	N(1)-C(1)-C(5)	123.6 (2)
C(3)-C(4)-C(8)	111.8 (2)	C(5)-C(1)-C(2)	121.4 (2)
C(3)-C(4)-C(9)	110.7 (2)	C(2)-C(1)-N(1)	115.0 (2)
N(3)-C(4)-C(8)	108.3 (2)	C(1)-C(2)-C(7)	109.0 (2)
N(3)-C(4)-C(9)	111.1 (2)	C(1)-C(2)-C(6)	111.8 (2)
C(8)-C(4)-C(9)	110.7 (2)	C(1)-C(2)-N(2)	103.8 (2)
N(1)-Ni-N(2)	83.1 (1)	C(6)-C(2)-C(7)	111.2 (2)
N(2)-Ni-N(3)	86.7 (1)	C(6)-C(2)-N(2)	109.7 (2)
N(3)-Ni-O(1)	87.3 (1)	C(7)-C(2)-N(2)	111.1 (2)
O(1)-Ni-N(1)	102.8 (1)	Ni-N(2)-C(2)	109.7 (1)
O(1)-Ni-N(2)	173.8 (1)	Ni-N(2)-C(3)	110.4 (1)
N(1)-Ni-N(3)	168.9 (1)	C(2)-N(2)-C(3)	117.6 (2)
O(1)-N(1)-Ni	127.8 (1)	N(2)-C(3)-C(4)	107.9 (2)
O(1)-N(1)-C(1)	115.6 (2)	Ni-N(3)-C(4)	111.1 (1)
C(1)-N(1)-Ni	116.6 (2)	Ni-O(1)-N(1)	125.3 (1)

2-methyl-3-butanone oximato)nickel(II) ion $[\text{Ni}(\text{AO})_2\text{-H}]^{+11}$, the Ni-N(oxime) distance (1.861 (2) Å) is significantly shorter than the Ni-N(amine) distances of 1.872 and 1.913 Å. The average Ni-N(oxime) distance of 1.865 (2) Å¹¹ is in excellent agreement with that bond distance in this complex. This value also agrees well with that found for various nickel dioximes.¹² However, the average Ni-N(amine) distance in $[\text{Ni}(\text{AO})_2\text{-H}]^+$ of 1.908 (1) Å suggests that the Ni-N(3) distance of 1.913 (2) Å represents a "normal" Ni-N(amine) distance while the 1.872 (2) Å Ni-N(2) is abnormally short. Associated with this shortening of the Ni-N(2) bond is what appears to be an unusually large C(2)-N(2)-C(3) angle of 117.6 (2)° since the angles around N2 would be expected to approach tetrahedral. Indeed the Ni-N(2)-C(2) and Ni-N(2)-C(3) angles are 109.7 (1) and 110.4 (1)°, respectively. Apparently the steric requirements of the ligand geometry are responsible for both of these unusual effects. The difference in Ni-N(oxime) distance (1.861 (2) Å) and Ni-O(oxime) distance (1.835 (2) Å) is comparable to that found (0.02 Å) for a copper complex with bridging oximes.¹³

Coordination of both ends of the oxime group to metal atoms does not appear to have a large effect on the N-O

bond since the N-O distance of 1.365 (3) Å is only slightly longer than the 1.340 (5) Å average N-O distance in $[\text{Ni}(\text{AO})_2\text{-H}]^+$ and the values of 1.35-1.36 Å observed for various metal dioximes where the oxime groups are coordinated to the metal through the nitrogen only.¹² The adjacent multiple C-N bond distance (1.289 (3) Å) is also comparable to that in $[\text{Ni}(\text{AO})_2\text{-H}]^+$ (1.288 (2) Å) and in metal dioximes. All other ligand bond distances are nearly normal with the expected changes in bond distances with hybridization evident. There are slight variations in the C-N(amine) distances for which no simple explanation is evident.

The bond angles about each nickel are not ideal square-planar angles, ranging from 83.1 to 102.8°. The 102.8° angle is associated with the six-membered nickel-oxime ring and is probably affected markedly by the steric requirements of the ring. For example the Ni-N(oxime)-O(oxime) angle of 127.8 (1)° is considerably larger than the 122.5 (2)° angle observed in $[\text{Ni}(\text{AO})_2\text{-H}]^+$. The deviation of the N(1)-Ni-N(3) angle (168.9 (1)°) from 180° is probably largely due to the ligand strain. Note also that the C(2)-N(2)-C(3) angle has opened to 117.6 (2)° minimizing the deviation of the N(1)-Ni-N(3) angle from 180°.

Conclusions

The interaction of this diamine oxime (BnAO) ligand with Ni(II) in water yields predominantly a dimeric ion in which two ligands bind together two metal ions using four ligand positions: the two amines and both the N and the O of the oxime group. This statement is based upon the similarity of the pmr spectra, the electronic spectra, and the ir spectra in water with those in organic solvents which are consistent with the solid structure. Coordination around each nickel is nearly planar with the oxime NO groups bridging. The Ni-Ni distance of 3.631 (2) Å is too long for significant interaction. The dimeric ion is essentially diamagnetic, but a residual paramagnetism may be real and imply incomplete spin pairing. Some similar structures were postulated by Liu and Liu¹⁴ for the interaction of pyridine-2-carbaldoxime with Cu(II) and Pd(II). In the dimer studied by Ginsberg, Sherwood, Brookes, and Martin $[\text{Ni}_2(\text{en})_4(\text{SCN})_2]\text{I}_2$ ¹⁵ the thiocyanate ions bridge the two octahedral metal ion centers, and while the Ni-Ni distance was too large (5.8 Å) for direct interaction, parallel spin coupling through the SCN bridge was found. The molecule ion was ferromagnetic with $J = 6 \text{ cm}^{-1}$.

While the solid structure is highly interesting, it coupled with chemical and spectral interpretations suggest that there is an abnormally large tendency toward dimerization without apparent reason. A more "normal" interaction would have been the formation of the octahedral bis complex or the planar mono(diamine oxime)quo complex. There is no indication of the former from spectral studies and one is not able with present data to determine accurately the fraction in the latter present at equilibrium. Equilibrium studies directed toward establishing the nature of all solution species and the magnitude of the dimerization constant in both the Ni(II) and Cu(II) systems are anticipated.

Registry No. $[\text{Ni}_2(\text{BnAO-H})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$, 51922-75-9.

Supplementary Material Available. A listing of structure factor amplitudes and Table VII, giving the rms displacements, will appear

(12) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953); R. K. Murmann and E. O. Schlemper, *ibid.*, **23**, 667 (1967).

(13) P. F. Ross, R. K. Murmann, and E. O. Schlemper, *Acta Crystallogr., Sect. B*, **30**, 1120 (1974).

(14) C. F. Liu and C. H. Liu in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961.

(15) A. P. Ginsberg, R. C. Sherwood, R. W. Brookes, and R. L. Martin, *J. Amer. Chem. Soc.*, **93**, 5928 (1971).

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Metal Ion-Aromatic Complexes. XV. Synthesis, Structure, and Bonding of $\pi\text{-C}_6\text{H}_6\text{Pb}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$

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Received May 29, 1974

AIC40347P

The synthesis of $\pi\text{-C}_6\text{H}_6\text{Pb}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$ has been accomplished and its crystal structure determined. The local environment of the Pb(II) is that of a distorted pentagonal bipyramid (6Cl) with an axial coordination site occupied by the center of a benzene ring. The remaining benzene is a molecule of solvation far removed from the metal. The overall structure is described as a chain in which AlCl_4^- tetrahedra are bridged together by Pb(II) and the other AlCl_4^- behaves as a chelating ligand to form an axial and an equatorial Pb-Cl bond. The Pb-Cl distances vary from 2.854 (8) to 3.218 (9) Å. The average Pb-C (bound) distance is 3.11 (4) Å and the Pb-center of ring distance is 2.77 (4) Å. A qualitative molecular orbital model is presented and adequately accounts for many of the Pb(II) coordination features. The crystal data are: monoclinic $P2_1/m$, $a = 11.365$ (1) Å, $b = 17.307$ (2) Å, $c = 12.707$ (2) Å, $\beta = 110.14$ (1)°, $\lambda = 0.71068$ Å; $\rho_o = 1.7\text{--}2.0$ g cm⁻³, $\rho_c = 1.99$ g cm⁻³, $Z = 4$, $\pi\text{-C}_6\text{H}_6\text{Pb}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$, $\mu = 80.6$ cm⁻¹. The structure was determined from 2075 countermeasured intensity data at room temperature and refined by full matrix least squares including anomalous dispersion corrections for Pb, Cl, and Al, as well as anisotropic temperature factors for these same atoms. The rings were refined as rigid units with isotropic temperature factors. The refinement converged to a final R of 0.073.

Introduction

Weakly bound complexes between metal ions and aromatic molecules have been known for some time, particularly for Ag(I).^{1a} A sufficiently large number of these complexes have been isolated, characterized, and crystal structures solved to make some statements as to the factors involved in their formation. Some of these factors follow. (1) A soft metal ion, a low oxidation state, e.g., Ag(I),¹ Cu(I),²⁻⁴ Ga(I),⁵ Sn(II),^{6,7} Hg(I),⁸ Pb(II),⁹ and Tl(I).⁹ This requirement is due at least in part to the fact that the higher oxidation states are such good electron acceptors that reactions involving these ions inevitably lead to reactions of the aromatic moiety, polymerization, decomposition, etc. In addition, reactions with the transition metals lead either to totally different types of benzene adducts such as dibenzenechromium or again to decomposition products. (2) The

anion must be the anion of a strong acid such as ClO_4^- ,^{1a,c-g} AlCl_4^- ,^{1b,2,5-9} BF_4^- ,¹⁰ $\text{F}_3\text{C}_2\text{O}_2^-$,⁴ and F_3CSO_3^- .³ One of the functions of the anion is to decrease the lattice energy and decrease the anion-cation binding so that the complex may be more readily formed; e.g., CuCl does not form a complex with benzene, but Cu(I) does with all the anions mentioned above. The other is to open the structure so that the aromatic molecule can more easily approach the metal ion. Nevertheless, several structure determinations have shown that cation-anion interactions can be important in the stabilization of these structures.¹⁻⁷ A perhaps surprising feature of many of these metal ion-aromatic complexes is that regardless of the extent of interaction between metal ion and anion, the geometry of the metal ion-aromatic complex can be correctly predicted based only upon the available s or p acceptor orbitals and the filled benzene π MO's. As part of the study of metal ion-aromatic systems, we wish to report here the preparation and crystal structure of $\pi\text{-C}_6\text{H}_6\text{Pb}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$. Our purpose here is twofold, one chemical and the other structural. Although the present compound is isomorphous *vide infra* with the corresponding Sn(II) compound, it is of interest to examine in detail the changes in the M-Cl distances and in the M(II) coordination sphere in going from Sn(II) to Pb(II). In addition, the refinement of the present structure will give us a guide [since it is closely related to the Sn(II) structure] as to how well we may be able to determine the structures of known compounds such as $(\text{HgAlCl}_4)_2\cdot 2\text{C}_6\text{H}_6$,⁸ $\text{Tl}^+\text{C}_6\text{H}_6\text{AlCl}_4^-$,⁹ and $\text{BiCl}_2\text{AlCl}_4\cdot\text{C}_6\text{H}_6$.⁹ Although we and others have determined structures with heavy atoms, e.g., Ir^{11,12} or Pt,^{13,14} the $\text{MAlCl}_4\cdot\text{C}_6\text{H}_6$

(1) (a) E. H. Griffith and E. L. Amma, *J. Amer. Chem. Soc.*, **93**, 3167 (1971), and references therein; (b) R. W. Turner and E. L. Amma, *ibid.*, **88**, 3243 (1966); (c) I. F. Taylor, Jr., E. A. Hall, and E. L. Amma, *ibid.*, **91**, 5745 (1969); (d) E. A. Hall and E. L. Amma, *ibid.*, **91**, 6538 (1969); E. H. Griffith and E. L. Amma, *ibid.*, **96**, 743 (1974); (e) I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1442 (1970); (f) P. F. Rodesiler and E. L. Amma, *Inorg. Chem.*, **11**, 388 (1972); (g) P. F. Rodesiler, E. H. Griffith, and E. L. Amma, *J. Amer. Chem. Soc.*, **94**, 761 (1972).

(2) (a) E. L. Amma and R. W. Turner, *J. Amer. Chem. Soc.*, **85**, 4046 (1963); (b) R. W. Turner and E. L. Amma, *ibid.*, **88**, 1877 (1966).

(3) (a) R. G. Solomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 559 (1972); (b) M. B. Dines and P. H. Bird, *ibid.*, 12 (1973).

(4) P. F. Rodesiler and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, in press.

(5) R. E. Rundle and J. D. Corbett, *J. Amer. Chem. Soc.*, **79**, 757 (1957).

(6) H. Luth and E. L. Amma, *J. Amer. Chem. Soc.*, **91**, 7515 (1969).

(7) M. S. Weininger, P. F. Rodesiler, A. G. Gash, and E. L. Amma, *J. Amer. Chem. Soc.*, **94**, 2135 (1972).

(8) R. W. Turner and E. L. Amma, *J. Inorg. Nucl. Chem.*, **28**, 2411 (1966).

(9) Th. Auel and E. L. Amma, *J. Amer. Chem. Soc.*, **90**, 5941 (1968).

(10) E. A. H. Griffith and E. L. Amma, unpublished results.

(11) M. S. Weininger, I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1172 (1971).

(12) J. A. McGinney, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(13) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).