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Crystal Structure of Tetrakis(*o*-phenylenediamine)nickel(II) Chloride-Bis(*o*-phenylenediamine) Adduct, $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$: a Crystal Containing Bidentate, Monodentate, and Toothless OPDA

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The crystal structure of the tetrakis(*o*-phenylenediamine)nickel(II) chloride-bis(*o*-phenylenediamine) adduct, $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$, has been determined using a Syntex $P\bar{1}$ X-ray diffractometer. The compound which normally forms twinned crystals is monoclinic, with $a = 12.703$ (12) Å, $b = 14.111$ (9) Å, $c = 10.796$ (7) Å, $\beta = 102.33$ (7)°; space group $P2_1/c$; $Z = 2$. The twinned data have been resolved and the structure refined by least-squares techniques using anisotropic thermal parameters to a conventional R factor of 0.086. The nickel cation is six-coordinate, binding two bidentate OPDA ligands and two trans monodentate OPDA ligands. Two molecules of OPDA are not coordinated and serve only as part of the extensive hydrogen-bonding network among complex cations, free OPDA, and chloride anions. The structure of the cation in $[Ni(OPDA)_4]Cl_2$ is apparently the same as that found here.

Introduction

In recent years there have been numerous reports in the literature[1-11] which have shown that certain surface-active species, such as Cl^-, SCN^-, organic amines, etc., adsorbed on electrodes can act to increase the heterogeneous electron-transfer rates of various transition metal ion redox reactions (electrocatalysis) in aqueous media. One very striking example is the effect of adsorbed *o*-phenylenediamine, OPDA, on Hg electrodes to increase the apparent heterogeneous electron-transfer rate constant, k_s, for the reduction of $[Ni(H_2O)_6]^{2+}$ by approximately eight orders of magnitude.[9,10] While extensive electrochemical kinetic studies have been carried out on this system, it has not been possible to determine the nature of the easily reduced intermediate complex that has been demonstrated to form only on the electrode surface during this reaction.[9,10] In an attempt to infer the structure of this intermediate we are synthesizing various $[Ni(OPDA)_n]^{2+}$ complexes ($n = 1$-6) and studying their electron-transfer kinetics in nonaqueous solvent systems in which the complexes are stable. We wish to determine what coordination geometries of these complexes[11] have low activation energies for reduction and to correlate ligand-exchange kinetics with the electron-transfer activation energies.[12]

One of the complexes[13-15] we have synthesized has the empirical formula $Ni(OPDA)_6Cl_2$ and had previously been suggested[13] to bind each of the six OPDA molecules as a unidentate ligand, based on ir, uv-vis, dta, and tga measurements. Since the proposed structure seemed somewhat dubious and since there is little structural information about the mode of binding of OPDA ligands, we have determined the structure of this complex and report it here.

Experimental Section

Preparation of $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$. Practical grade *o*-phenylenediamine (Matheson Coleman and Bell) was recrystallized from ethanol, vacuum-dried, and sublimed four times. A solution of *o*-phenylenediamine, OPDA, in ethanol with excess OPDA solid was prepared in a glove bag (N_2 atmosphere). An ethanolic solution of hexaaquonickel(II) chloride was added dropwise without stirring such that the OPDA:Ni^{2+} ratio was greater than 6:1. Small, violet[16] crystals of product percipitated and were filtered off with some undissolved OPDA. After drying, the violet crystals were manually separated from unreacted OPDA. Other preparative procedures[13] (use of stirring, more dilute solution with all OPDA dissolved, etc.) lead to the formation of violet powders of $Ni(OPDA)_6Cl_2$. Attempts to recrystallize the powder from ethanol, methanol, dimethylformamide, and acetonitrile were unsuccessful. The manually separated crystals (dec pt *ca.* 180°) of formula $Ni(OPDA)_6Cl_2$ were analyzed. *Anal.* Calcd for $Ni(C_6H_8N_2)_6Cl_2$: C, 55.54; H, 6.22; N, 21.59. Found: C, 55.71; H, 6.30; N, 21.59. The ir spectrum (measured on a Beckman IR-12) for the NH stretching region has the same number of bands and approximately the same band positions as those published (ir-ref 13: 3383, 3317, 3225, 3185, 3150, 3095, 3050 cm^{-1}; this compound: 3405, 3310, 3235, 3200, 3150, 3100, 3050 cm^{-1}). A dta-tga study of our crystalline material which contained some OPDA solid as a contaminant gave endotherms at 99 (OPDA melting), 181, and 232° (previously reported[13] 181 and 234°) with the onset of weight loss at *ca.* 150° in agreement with that previously reported. Thus we conclude that the two materials are the same crystalline compound.

X-Ray Characterization. Several of the violet, needle-shaped crystals of the formula $Ni(OPDA)_6Cl_2$ were mounted on glass fibers such that the long dimension, c, was coincident with the fiber axis. Precession photographs of the $h0l$, $h1l$, $0kl$, and $1kl$ layers were taken (using Cu Kα radiation) for each of these and all of the crystals examined were found to be twinned by a pseudomirror operation about (100). The unit cell constants (*vide infra*) are such that in the $h1l$ photograph rows with $l = 2n$ contain spots which result from the superposition of reflections from both members of the twin whereas in rows with $l = 2n + 1$ the reflections from the second member of the twin occur halfway between those from the first. When proper account is taken of the twinning phenomena, the systematic absences of $h0l$ for l odd and $0k0$ for k odd are found, indicating the space group[17] as $P2_1/c$-C_{2h}^5 (No. 14).

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(14) E. J. Duff, *J. Chem. Soc. A*, 434 (1968).
(15) D. R. Marks, D. J. Phillips, and J. P. Redfern, *J. Chem. Soc. A*, 2013 (1968).

(16) Although the compound $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ studied here appears violet in the crystalline form under both fluorescent light and sunlight, a powder sample of this material appears violet in fluorescent light and pink in sunlight.

(17) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965.

Unit cell dimensions and intensity data were obtained from a crystal (0.52 × 0.16 × 0.15 mm) using a Syntex $P\bar{1}$ diffractometer with Mo Kα radiation (λ 0.71069 Å) and equipped with a graphite crystal monochromator. Fifteen reflections (all from one twin member) were precisely centered and lattice constants determined by a least-squares analysis of the measured 2θ values are $a = 12.703$ (12) Å, $b = 14.111$ (9) Å, $c = 10.796$ (7) Å, and $\beta = 102.33$ (7)°. All measurements were made at 21 ± 2°. Density measurements ($d_{measd} = 1.37$ (5) g/cm^3, neutral buoyancy in CH_2Cl_2-$CHCl_3$; $d_{calcd} = 1.34$ g/cm^3) indicated $Z = 2$, which requires that the nickel atom have $\bar{1}$ symmetry.

Intensity Data Collection. The intensity data are of three types for these twinned crystals: first, reflections from the first twin member with l odd; second, reflections with l even which contain the superposed data from both twin members; third, reflections from the second twin with l odd. For the superposed data, the indices of the reflection from the second member are obtained from the first by the following transformations: $h' = h + l/2$; $k' = k$; $l' = -l$. Two data sets were measured under previously described conditions,[18] a first set of 4546 reflections within the sphere $2\theta < 53°$ which contained the first two types of reflections given above and a second partial data set of 1500 reflections taken on the second twin member which contained the last two types of reflections given above. Since in the two data sets above those reflections with l odd contain information from a single twin member only, the ratio of the sum of the 670 common l odd reflections from twin one to the sum of 670 common l odd reflections from twin two gives a relative scale factor for the intensities from each twin. $I_{twin\ 2} = 0.792 I_{twin\ 1}$. Using this scale factor the superposed data may be separated according to the formula

$$I_{h,k,l} = \frac{MI_{h,k,l} - 0.792 MI_{h+l/2,k,\bar{l}}}{1 - 0.792^2}$$

where $MI_{h,k,l}$ is the measured intensity for the reflection with indices h, k, l in the first twin and $MI_{h+l/2,k,\bar{l}}$ is the measured intensity for the reflection with the indices $h + l/2, k, \bar{l}$ in the same twin. Thus, it was possible to produce the single set of intensity data which would be observed for a nontwinned crystal. These data were then processed in the normal fashion using the X-RAY 67 program package,[19] with the exception that all l odd reflections were given one scale factor, all l even ($l \neq 0$) reflections a second scale factor, and all $l = 0$ reflections a third scale factor for the least-squares refinement. The data used for refinement included 1784 reflections with l odd, 1739 with l even ($l \neq 0$), and 53 with $l = 0$. Of these 1166, 1081, and 47 respectively had $F_o > 3\sigma F_o$ and were considered as observed. The linear absorption coefficient, μ, of the compound for Mo Kα radiation is 6.87 cm^{-1}. Minimum and maximum path lengths through the crystal, mounted with its long dimension coincident with the glass fiber axis, were estimated to be 0.15 and 0.25 mm, respectively, under the conditions of data collection. The maximum relative error in F_o due to absorption is thus less than 2% and no corrections were made.

Solution and Refinement of Structure

A Patterson map was computed using the observed reflections and it confirmed the choice of position 2a (0, 0, 0; 0, 1/2, 1/2) for the nickel atom and indicated the position of the chlorine atom. Subsequent Fourier electron density maps computed using signs for F_o determined from the trial structure gave the positions of the remaining nonhydrogen atoms. Least-squares refinement using unit weights and isotropic temperature parameters gave a conventional residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.122$. Hydrogen atoms were added at the calculated positions[20,21] (C-H = 1.08 Å; N-H = 1.00 Å) for all carbon-bound hydrogen atoms and for those nitrogen atoms with geometry fixed by a nitrogen-metal bond. The positions of the hydrogen atoms bound to uncoordinated nitrogen atoms could not be clearly ascertained from difference electron density maps. Refinement was continued using anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors of 4.0 Å^2 for the hydrogen atoms. A weighting scheme of the form[22] $w = 1.0/(A + F_o + B^*F_o^2 + C^*F_o^3)$ was introduced where $A = 80.3$ (=10^*F_{min}), $B = 2.11 \times 10^{-4}$ (=$0.04/F_{max}$), and $C = 4.52 \times 10^{-4}$ (=$15/F_{max}^2$). Convergence was approached at $R = 0.086$ varying all parameters except those of the hydrogen atoms. The discrepancy between F_o and F_c values may be further subdivided into R_{odd}, R_{even}, and R_0 for reflections with l odd, l even ($l \neq 0$), and $l = 0$, respectively. Weighted residuals may be defined analogously, where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The following values were obtained in the last cycle of least-squares refinement: $R_{odd} = 0.051$, $R_{even} = 0.123$, $R_0 = 0.055$, $R_w = 0.106$, $R_{w_{odd}} = 0.066$, $R_{w_{even}} = 0.161$, $R_{w_0} = 0.066$. The large discrepancy for l even data indicates a less than ideal resolution of the superposed data. However, the relatively low values for R_{odd}, R_0, $R_{w_{odd}}$, and R_{w_0} substantiate the overall validity of the structure determination. Examination of R_w computed for groups of reflections ordered in increasing values of (sin θ)/λ as well as F_o showed no systematic trends.[22] During the last cycle of refinement no parameter varied by more than 0.6σ except the U_{11} value of C(17) which changed by 0.7σ. A final difference map showed a largest residual peak of less than one-tenth the height of a carbon atom peak on the same scale. The scattering curves used were those for Ni, Cl, N, C,[23] and H.[21] No corrections were made for extinction or anomalous scattering.

Results and Discussion

The final atomic positional parameters and the estimated standard deviations for $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ are listed in Table I. The anisotropic temperature factors for the nonhydrogen atoms are listed in Table II and the associated thermal vibrational ellipsoids may be seen in Figures 1 and 2 which have been drawn using ORTEP II.[24] The root-mean-square amplitudes of vibration for the nonhydrogen atoms are given in Table III. Bond lengths and bond angles are presented in Tables IV and V, respectively.

Coordination Geometry. The structure of the cation $[Ni(OPDA)_4]^{2+}$ is shown in Figure 1. The nickel atom is six-coordinate with the *o*-phenylenediamine functioning as both a mono- and bidentate ligand. Thus although in the crystalline compound there are 12 amine groups present, only six of these are coordinated. Two molecules of OPDA are not coordinated at all (toothless) but are merely present as molecules of crystallization. The four nitrogen atoms from the two bidentate OPDA molecules form a rectangular plane (*vide infra*) containing the nickel atom at the center. The two monodentate OPDA ligands are positioned trans to each other to complete the tetragonally distorted "octahedral" coordination about the nickel atom.

The two bidentate OPDA ligands are nearly coplanar, although not exactly so. They may be considered to be hinged about a line passing through the two nitrogen atoms, such that they are at an angle of 3.2° to the plane of the central four nitrogen atoms and the nickel atom and are bent away from the neighboring monodentate OPDA ligand. All of the OPDA moieties are nearly planar and a table containing the equations of the best least-squares planes and the distances of the atoms from their respective planes is available (*vide infra*).

There are two obvious causes of distortion of the nickel

(18) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, 12, 2690 (1973).

(19) All computations were carried out using a local version of XRAY 67: J. M. Stewart, University of Maryland, crystallographic computer system.

(20) The subprogram LOADAT has been modified to include an atom-positioning function. This is run after every cycle of least squares to reposition the fixed hydrogen atoms.

(21) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973), commented that the X-H distances used here were undoubtedly too long; note however, that the spherically symmetric floated scattering curves [R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965)] used here attempt to compensate for the discrepancy between the position of the centroid of electron density about the hydrogen atom and the nuclear position, and the error introduced is likely to be insignificant.

(22) The values of A, B, and C are chosen using the WTLSSQ routine in XRAY 67 to minimize variation in $w\Delta^2$ computed for groups of reflections ordered on increasing values of F_o.

(23) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(24) C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration," ORTEP II, Report ORNL-3794, 2nd Revision, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970. The ellipsoids are plotted at 60% probability in both figures.

Table I. Fractional Atomic Positional Parameters[a,b]

	x	y	z
Ni	0.000	0.000	0.000
Cl	−0.0036 (2)	0.2289 (2)	0.2832 (2)
N(1)	0.1114 (5)	0.0514 (4)	0.1584 (6)
N(2)	0.1029 (5)	0.0709 (4)	−0.0981 (6)
N(3)	−0.0960 (5)	0.1357 (4)	−0.0022 (6)
N(4)	−0.2185 (6)	0.0938 (5)	0.1846 (6)
N(5)	0.0868 (9)	−0.0592 (9)	0.3983 (9)
N(6)	0.1573 (9)	0.1113 (8)	0.5334 (11)
C(1)	0.1984 (6)	0.1009 (5)	0.1187 (8)
C(2)	0.1935 (6)	0.1133 (5)	−0.0086 (8)
C(3)	0.2743 (7)	0.1623 (6)	−0.0492 (10)
C(4)	0.3604 (7)	0.1994 (7)	0.0386 (11)
C(5)	0.3672 (8)	0.1845 (7)	0.1657 (11)
C(6)	0.2866 (7)	0.1360 (6)	0.2072 (8)
C(7)	−0.2122 (6)	0.1292 (5)	−0.0345 (7)
C(8)	−0.2726 (7)	0.1080 (5)	0.0555 (8)
C(9)	−0.3825 (7)	0.0957 (7)	0.0169 (9)
C(10)	−0.4340 (8)	0.1040 (8)	−0.1095 (10)
C(11)	−0.3740 (8)	0.1265 (8)	−0.1977 (9)
C(12)	−0.2650 (7)	0.1403 (6)	−0.1616 (8)
C(13)	0.1928 (9)	−0.0532 (7)	0.4767 (8)
C(14)	0.2280 (9)	0.0349 (7)	0.5352 (8)
C(15)	0.3337 (9)	0.0411 (7)	0.6021 (10)
C(16)	0.4037 (11)	−0.0359 (9)	0.6122 (11)
C(17)	0.3660 (12)	−0.1198 (9)	0.5582 (11)
C(18)	0.2675 (14)	−0.1276 (7)	0.4909 (10)
H(1)N(1)	0.1412[c]	−0.0030	0.2142
H(2)N(1)	0.0738	0.0959	0.2067
H(3)N(2)	0.0619	0.1220	−0.1518
H(4)N(2)	0.1311	0.0248	−0.1533
H(5)N(3)	−0.0758	0.1641	0.0844
H(6)N(3)	−0.0739	0.1794	−0.0649
H(7)C(3)	0.2700	0.1719	−0.1494
H(8)C(4)	0.4220	0.2398	0.0072
H(9)C(5)	0.4357	0.2110	0.2334
H(10)C(6)	0.2922	0.1252	0.3076
H(11)C(9)	−0.4292	0.0793	0.0866
H(12)C(10)	−0.5201	0.0932	−0.1385
H(13)C(11)	−0.4128	0.1333	−0.2963
H(14)C(12)	−0.2195	0.1598	−0.2315
H(15)C(15)	0.3630	0.1070	0.6482
H(16)C(16)	0.4866	−0.0291	0.6613
H(17)C(17)	0.4181	−0.1811	0.5720
H(18)C(18)	0.2427	−0.1941	0.4443

[a] The estimated errors in the last digit are given in parentheses. This form is used throughout. [b] The numbering scheme for the atoms of the cation is shown in Figure 1. N(5), N(6), and C(13)–C(18) constitute the free OPDA molecule. [c] The hydrogen atom positions are calculated and not refined. Thus they have no estimated errors.

coordination sphere from an octahedral geometry. First the rather inflexible nature of the OPDA ring system determines the bite of this ligand in bidentate coordination. The N-N distance within an OPDA ligand is 2.761 (9) Å. This with the average[25] Ni-N distance of 2.102 (7) Å for the bidentate OPDA gives an intraligand N-Ni-N angle of 82.1 (3)° whereas the N-Ni-N angle between ligands in the equatorial plane is 97.9 (3)°. A detailed comparison to coordinated *N,N,N′N′*-tetramethyl-*o*-phenylenediamine, Me_4OPDA, in Ni(Me_4-OPDA)$(NO_3)_2$[26], Ni(Me_4OPDA)$(H_2O)_2Cl_2$,[27] and Ni(Me_4-OPDA)$(H_2O)_2Br_2$[27] and to the *o*-phenylenediamino ligand in $Ni(C_6H_4(NH)_2)_2$[28] is given in Table VI. The differences in the last case may reasonably be ascribed to the aromatic nature of the nickel-nitrogen ring system in that compound.

The second distortion from octahedral geometry involves

(25) The error in a mean value has been calculated to be either the largest of the individual esd's or $\sigma_{\bar{d}} = [\Sigma_{i=1}{}^{n}(d_i - \bar{d})^2/(n-1)]^{1/2}$, whichever is larger.

(26) G. Bombieri, E. Forsellini, R. Graziani, and E. Tondello, *J. Chem. Soc. A*, 3349 (1970).

(27) G. Bombieri, E. Forsellini, G. Bandoli, L. Sindellari, R. Graziani, and C. Panattoni, *Inorg. Chim. Acta*, 2, 27 (1968).

(28) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, 7, 2300 (1968).

Table II. Anisotropic[a] Thermal Parameters (×10⁴)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	28 (1)	25 (1)	29 (1)	−02 (1)	09 (1)	−01 (1)
Cl	53 (1)	46 (1)	56 (1)	06 (1)	04 (1)	−24 (1)
N(1)	38 (3)	29 (3)	36 (3)	−04 (3)	04 (3)	02 (2)
N(2)	36 (3)	31 (3)	42 (4)	−0 (3)	15 (3)	05 (3)
N(3)	37 (3)	32 (3)	34 (3)	−01 (3)	09 (3)	03 (3)
N(4)	50 (4)	47 (4)	37 (4)	05 (3)	16 (3)	03 (3)
N(5)	95 (8)	119 (9)	47 (5)	−49 (7)	−06 (5)	15 (5)
N(6)	93 (8)	85 (7)	83 (7)	40 (6)	24 (6)	13 (6)
C(1)	26 (4)	25 (3)	57 (5)	03 (3)	05 (3)	−03 (3)
C(2)	27 (4)	30 (4)	49 (4)	01 (3)	11 (3)	02 (3)
C(3)	45 (5)	41 (4)	72 (6)	00 (4)	20 (4)	06 (4)
C(4)	39 (5)	43 (5)	84 (7)	−09 (4)	15 (4)	−04 (5)
C(5)	46 (5)	46 (5)	77 (7)	−10 (4)	01 (5)	−14 (5)
C(6)	42 (5)	46 (5)	51 (5)	−09 (4)	03 (4)	−11 (4)
C(7)	32 (4)	27 (3)	40 (4)	03 (3)	10 (3)	−06 (3)
C(8)	43 (4)	33 (4)	46 (4)	03 (3)	21 (4)	04 (3)
C(9)	42 (5)	53 (5)	62 (6)	−05 (4)	23 (4)	−04 (4)
C(10)	38 (5)	70 (7)	65 (6)	−01 (5)	09 (4)	−08 (5)
C(11)	54 (6)	67 (6)	43 (5)	02 (5)	−09 (4)	−02 (4)
C(12)	46 (5)	42 (4)	36 (4)	05 (4)	09 (3)	−04 (3)
C(13)	84 (8)	61 (6)	35 (4)	−27 (6)	13 (5)	10 (4)
C(14)	69 (6)	55 (5)	35 (4)	−06 (5)	10 (4)	05 (4)
C(15)	76 (7)	45 (5)	54 (6)	−12 (5)	07 (5)	05 (4)
C(16)	80 (8)	65 (7)	64 (7)	−03 (6)	07 (6)	11 (5)
C(17)	120 (11)	66 (8)	53 (6)	20 (7)	29 (7)	12 (6)
C(18)	164 (14)	42 (5)	45 (6)	−11 (7)	31 (7)	01 (5)

[a] The thermal parameters are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

Table III. Root-Mean-Square Amplitudes of Vibration, Å (×10³)

Atom	Min	Mean	Max	Atom	Min	Mean	Max
Ni	158	167	178	C(6)	187	221	243
Cl	195	221	270	C(7)	161	177	206
N(1)	166	182	211	C(8)	180	206	216
N(2)	175	189	208	C(9)	204	231	250
N(3)	175	182	199	C(10)	194	255	270
N(4)	192	216	228	C(11)	187	258	263
N(5)	209	291	375	C(12)	183	203	226
N(6)	257	296	332	C(13)	185	235	306
C(1)	154	163	245	C(14)	185	234	269
C(2)	164	174	224	C(15)	208	228	290
C(3)	201	213	271	C(16)	240	259	300
C(4)	190	214	295	C(17)	225	257	351
C(5)	196	225	292	C(18)	204	211	409

Table IV. Bond Lengths (Å)

Ni-N(1)	2.102 (6)	Ni-N(2)	2.103 (7)
Ni-N(3)	2.267 (6)	N(1)-C(1)	1.449 (11)
N(2)-C(2)	1.462 (9)	N(3)-C(7)	1.446 (10)
N(4)-C(8)	1.430 (10)	N(5)-C(13)	1.431 (15)
N(6)-C(14)	1.401 (16)	C(1)-C(6)	1.399 (11)
C(1)-C(2)	1.373 (12)	C(3)-C(4)	1.388 (13)
C(2)-C(3)	1.385 (13)	C(5)-C(6)	1.383 (15)
C(4)-C(5)	1.372 (16)	C(7)-C(12)	1.402 (10)
C(7)-C(8)	1.393 (12)	C(9)-C(10)	1.387 (14)
C(8)-C(9)	1.380 (12)	C(11)-C(12)	1.370 (13)
C(10)-C(11)	1.378 (16)	C(13)-C(18)	1.402 (18)
C(13)-C(14)	1.422 (14)	C(15)-C(16)	1.393 (17)
C(14)-C(15)	1.385 (15)	C(17)-C(18)	1.311 (21)
C(16)-C(17)	1.360 (17)		

the difference between the nickel-nitrogen bond length found for the two trans, monodentate, axial OPDA moieties, 2.267 (6) Å, and the equatorial nickel-nitrogen bond length, 2.102 (7) Å. It appears that this difference represents a lengthening of the axial bonds due to steric crowding about the nickel atom. The conformation of the monodentate OPDA ligand is controlled by the nickel-nitrogen bond length, 2.267 (9) Å, the nickel-nitrogen-carbon bond angle, 118.0 (4)°, an intracationic hydrogen bond, N(4)· ·N(2)

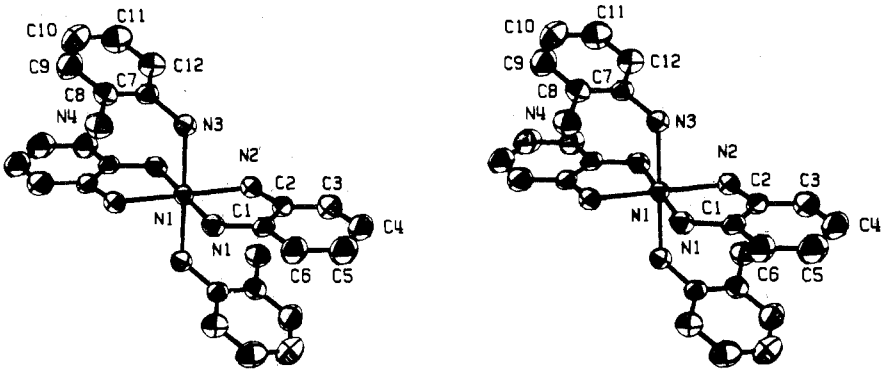

Figure 1. A stereodiagram showing the structure of the $[Ni(OPDA)_4]^{2+}$ cation.

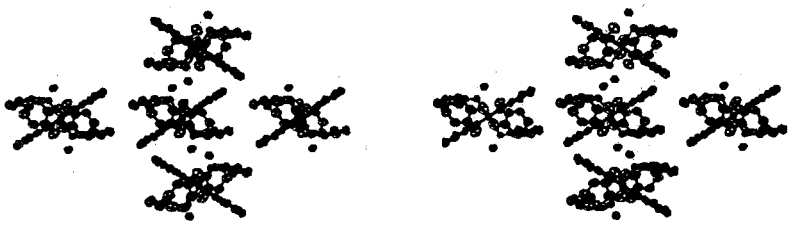

Figure 2. Stereoscopic view down the *c* axis showing the contents of two unit cells.

Table V. Bond Angles (deg)

N(1)-Ni-N(2)	82.1 (3)	N(1)-Ni-N(3)	89.1 (2)
N(2)-Ni-N(3)	89.1 (2)	N(1)-C(1)-C(2)	118.9 (6)
N(2)-C(2)-C(1)	118.1 (7)	N(3)-C(7)-C(8)	122.1 (6)
N(4)-C(8)-C(7)	119.2 (7)	N(5)-C(13)-C(14)	118.8 (10)
N(6)-C(14)-C(13)	121.7 (10)	Ni-N(1)-C(1)	110.5 (5)
Ni-N(3)-C(3)	118.0 (4)	Ni-N(2)-C(2)	110.4 (5)
C(6)-C(1)-C(2)	119.8 (8)	C(1)-C(2)-C(3)	120.1 (7)
C(2)-C(3)-C(4)	120.1 (10)	C(3)-C(4)-C(5)	119.9 (10)
C(4)-C(5)-C(6)	120.4 (9)	C(5)-C(6)-C(1)	119.7 (9)
C(12)-C(7)-C(8)	119.1 (7)	C(7)-C(8)-C(9)	119.3 (8)
C(8)-C(9)-C(10)	121.4 (10)	C(9)-C(10)-C(11)	119.0 (9)
C(10)-C(11)-C(12)	120.7 (8)	C(11)-C(12)-C(7)	120.4 (9)
C(18)-C(13)-C(14)	117.6 (10)	C(13)-C(14)-C(15)	117.7 (9)
C(14)-C(15)-C(16)	121.6 (10)	C(15)-C(16)-C(17)	118.9 (12)
C(16)-C(17)-C(18)	121.2 (13)	C(17)-C(18)-C(13)	122.9 (11)

Table VI. Comparisons of Some *o*-Phenylenediamine-Nickel Complexes

	$Ni(OPDA)_6Cl_2$	$Ni(Me_4OPDA)X_2$ [a,26,27]	$Ni(C_6H_4(NH)_2)_2$ [28]
$Ni-N_{eq}$, Å	2.102 (6) 2.103 (7)	2.071 (4) (NO_3) 2.118 (9) (Cl) 2.151 (9) (Br)	1.832 (8)
N-C, Å	1.452 (9) (av)	1.494 (34)	1.38 (3)
C-C (av), Å	1.382 (23)	1.384 (21)	1.40 (3)
N- -N "bite," Å	2.761	2.86 (6)	2.49
N-Ni-N, deg	82.1 (0.3)	85.2 (1.1)	85.9 (0.2)
Ni-N-C, deg	110.5 (0.1) (av)	107.7 (1.4)	114.3 (1.7)
N-C-C^N, deg	118.5 (0.4) (av)	119.7 (9)	113.3 (1.8)

[a] For $Ni(Me_4OPDA)(NO_3)_2$ the two nitrate groups are each bidentate (see ref 26). For X = Br, Cl there are two cis X anions and two trans water ligands (see ref 27).

(*vide infra*), repulsion between the bidentate and monodentate OPDA rings (see Figure 1 and Table VII), and packing forces (see Figure 2). A comparison of typical nickel-nitrogen bond lengths given in Table VIII indicates that the nickel-nitrogen equatorial bond lengths are probably "normal" and the axial ones are "long."[29-71]

(29) The length of this Ni-N bond is only exceeded by the 2.317 and 2.285 Å values found for the axial (Ni-N) bonds found in bis(*N*-γ-dimethylaminopropylsalicylaldiminato)nickel(II) [M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 6, 490 (1967)] as being the longest Ni-N thus far reported.

Crystal Packing. The crystal packing is shown in Figure 2 which is a view of the contents of two unit cells looking down

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Table VII. Ring–Ring Contacts

Intracationic Ring–Ring Distances, Å

	N(3)	N(4)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)
N(1)'[b]	3.12	*a*	3.26	4.08	*a*	*a*	4.12	3.33
N(2)'	3.12	3.00	3.33	3.29	4.19	*a*	*a*	4.30
C(1)'	3.70	4.32	3.39	3.73	4.10	4.18	3.90	3.51
C(2)'	3.73	3.54	3.45	3.35	3.82	4.32	4.41	4.04
C(3)'	*a*	3.91	4.32	3.82	3.88	4.44	*a*	*a*
C(4)'	*a*	*a*	*a*	*a*	4.22	4.41	*a*	*a*
C(5)'	*a*	*a*	*a*	*a*	4.44	4.23	4.40	*a*
C(6)'	*a*	*a*	4.20	4.44	4.39	4.12	3.88	3.93

Cation Ring–Free Ring Distances, Å

	N(5)	N(6)	C(13)	C(14)	C(15)	C(17)	C(18)
N(1)	*a*	4.05	3.68	4.03	*a*	*a*	4.49
N(3)'	3.93	*a*	*a*	*a*	*a*	*a*	*a*
C(1)	4.25	*a*	4.45	*a*	*a*	*a*	*a*
C(6)	*a*	4.21	4.30	4.03	4.39	*a*	*a*
C(11)'	*a*	*a*	4.29	*a*	*a*	3.92	3.70
C(12)'	3.93	*a*	3.91	*a*	*a*	4.21	3.55

[a] Distance greater than 4.50 Å. All other intra-ring distances are greater than 4.50 Å. [b] The prime indicates the position is generated by an inversion operation.

Table VIII. Typical Nickel–Nitrogen Bond Distances (Å)

Type	Average	Range	No. of cases	Ref
Oxime	1.84	1.83–1.95	11	30–36
Azo-azenido[a]	1.89	1.86–1.93	3	37, 38
Pyridine[b]	2.04	1.88–2.16	8	35, 39–42
"tren" (RR'R''N)	2.06	1.96–2.14	8	41, 43, 44
Phenanthroline	2.07	1.97–2.15	16	45–49
	2.04,[e] 2.10[f]			
Pyrrole[c]	2.09	2.08–2.13	9	42, 50–54
Isothiocyanate	2.10	2.04–2.15	4	55, 56
Ammonia (amine)	2.10	2.06–2.15	3	55, 57
Ethylenediamine[d]	2.12	1.91–2.23	49	30, 43, 44, 56 58–71

[a] Aromatic nitrogen systems. [b] Refers to substituted as well as bipyridine types. [c] Refers to imidazole, pyrazole, and bipyrrole types. [d] Includes propylenediamine. [e] Mono. [f] Tris.

the *c* axis. The isolated complex cations, chloride ions, and lattice molecules of OPDA are held together by a network of hydrogen bonds. Possible hydrogen bonds[72] are listed in Table IX. The chloride ion is surrounded by seven nitrogen atoms at distances ranging from 3.27 to 3.61 Å. Three of these involve nitrogen atoms of the complex cation in the same asymmetric unit, two involve nitrogen atoms of the neighboring cation generated by the glide plane, one involves a nitrogen atom on the lattice OPDA in the asymmetric unit, and the last involves a nitrogen atom on a neighboring free OPDA generated by the screw axis. Two other hydrogen bonds are noteworthy. One presumably utilizes the electron pair on N(4), the uncoordinated nitrogen atom of the monodentate OPDA ligand, to bind to one of the hydrogen atoms, H(4), on N(2), a coordinated nitrogen atom of a bidentate OPDA ligand of the same cation. The second appears to utilize the electron pair of N(5), on the free OPDA molecule, to bind H(1) on N(1) of the bidentate ligand.

Table IX. Possible Hydrogen Bonds

A–H···B	H···B[a]	A···B	∠AHB[b]
N(1)–H(2)···Cl	2.35	3.33	165
N(2)[c]–H(3)[c]···Cl	2.32	3.27	160
N(3)–H(5)···Cl	2.33	3.33	172
N(3)[c]–H(6)[c]···Cl	2.40	3.40	173
N(4) *e* Cl	*e*	3.31	*e*
N(5)[d] *e* Cl	*e*	3.61	*e*
N(6) *e* Cl	*e*	3.44	*e*
N(1)–H(1)···N(5)	2.37	3.10	129
N(2)–H(4)···N(4)	2.08	3.00	153

[a] Distances are given in angstroms. [b] Angles are given in degrees. [c] This atom generated by *c* glide at $y = 1/4$. [d] This atom generated by 2_1 at $x = 0, z = 1/4$. [e] The hydrogen atom in this set was not found.

The determination of the crystal structure of $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ allows several hypotheses concerning the behavior of this complex and the structure of $Ni(OPDA)_4Cl_2$. Marks, Phillips, and Redfern[13] correctly postulated that the complex formulated as $Ni(OPDA)_6Cl_2$ has uncoordinated amine groups. Although they considered the structure found here, they chose instead a model with six monodentate OPDA ligands. Their choice was based largely on the difference in tga and dta measurements for a sample of $Ni(OPDA)_6Cl_2$ and for a sample containing $Ni(OPDA)_4Br_2$ plus free OPDA. Since the uncoordinated OPDA in $Ni(OPDA)_6Cl_2$ is hydrogen bonded to both the chloride ion and the complex cation, it is not surprising that loss of OPDA takes place at higher temperatures for $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ than for the mixture containing solid OPDA and $[Ni(OPDA)_4]Br_2$ and that the melting endotherm at 108° of solid OPDA was not found for the complex which they formulated as $Ni(OPDA)_6Cl_2$. The structure of $[Ni(OPDA)_4]Cl_2$ may reasonably be expected to contain a $[Ni(OPDA)_4]^{2+}$ cation of the structure found here. The NH stretching region of the $[Ni(OPDA)_4]Cl_2$ ir spectrum is very similar to that of $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ with the exception that there are additional bands in the latter case which may be ascribed to the lattice OPDA molecules. The diffuse reflectance spectra of the two compounds are nearly identical. It is interesting to note that the solid $Ni(OPDA)_4Cl_2$ compound appears to be significantly less stable than $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ solid. The hydrogen-bonding network involving free OPDA, anions, and cations may be an important factor in giving added stability.

Finally we note that in the structure of $[Ni(OPDA)_4]^{2+}$ cation the free amine group N(4) is held relatively close to the nickel atom (N(4)–Ni = 3.61 Å) and that it is possible that the two bidentate and two monodentate ligands could interchange roles in a synchronous mechanism. Certainly the versatile nature of the OPDA ligand in terms of the ways in which it may coordinate must be of importance in the electron-transfer reaction of $[Ni(H_2O)_6]^{2+}$ with a Hg electrode containing adsorbed OPDA.

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Registry No. $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$, 51266-72-9; $Ni(OPDA)_6Cl_2$, 16999-86-3.

Supplementary Material Available. A listing of the structure factor amplitudes and a table of least-squares planes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1644.

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Crystal and Molecular Structure of Bis{perchlorato[2-(2-hydroxyethyl)imino-3-oximobutanato]aquocopper(II)}. A Copper(II) Dimer with Bridging Oxime Groups

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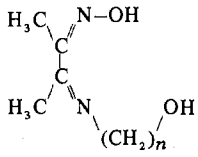
An unusual dimeric structure has been revealed by a single-crystal X-ray diffraction study of $CuL(ClO_4)(H_2O)$ (where L represents the anion of 2-(2-hydroxyethyl)imino-3-oximobutane). The dimer contains a centrosymmetric, nearly-planar six-membered ring formed by two copper atoms and two oxime (NO) groups. The Cu–N(oxime) and Cu–O(oxime) distances, 1.987 (5) and 1.870 (4) Å, respectively, indicate very strong coordination by both atoms of the oxime group, while the angles at N(oxime), Cu–N–O = 129.4 (3)°, and at O(oxime), Cu–O–N = 121.9 (3)°, are indicative of essentially sp^2 hybridization for the oxime atoms. The square-planar coordination of each copper atom is completed by a nitrogen atom (Cu–N = 1.928 (5) Å) and an oxygen atom (Cu–O = 2.038 (5) Å) of the tridentate ligand; there are also weak axial contacts to the water molecule (Cu–O = 2.492 (6) Å) and the perchlorate group (Cu–O = 2.89 (1) Å). The magnetic moment of zero (the compound shows only temperature-independent paramagnetism) is ascribed to superexchange through the N–O bridges. Crystal data are as follows: space group $P2_1/c$, $Z = 4$ formula units or 2 dimeric units; $a = 7.868$ (2), $b = 14.040$ (7), $c = 11.401$ (5) Å; $\beta = 112.73$ (4)°; $\rho_{calcd} = 1.85$ and $\rho_{obsd} = 1.83$ (2) g cm^{-3}. The structure has been refined by full-matrix least-squares refinement to unweighted (R) and weighted (R_w) residuals of 0.057 and 0.056, respectively, for the 1579 reflections above background ($I \geq 3\sigma(I)$).

Introduction

Ablov and coworkers recently reported[1] an interesting complex which was obtained from the reaction of copper(II) perchlorate and the ligand 2-(2-hydroxyethyl)imino-3-oximobutane (hereafter abbreviated HL), I. The complex $CuL(ClO_4)(H_2O)$ was reported to have a very low magnetic moment (0.41 BM at ambient temperature) characteristic of antiferromagnetic coupling in a polynuclear complex. Because of the possibility of highly unusual oxime bridges, we have investigated the structure of this complex and we have initiated a study of other transition metal complexes with this type of ligand. In this paper we report the details of a single-crystal X-ray diffraction study of $[CuL(ClO_4)(H_2O)]_2$, a dimeric compound with a planar, six-membered ring. A preliminary communication of these results has appeared.[2] We also report the preparation and properties of the analogous compound of 2-(3-hydroxypropyl)imino-3-oximobutane, $CuL'(ClO_4)(H_2O)$.



I
$n = 2$, HL
$n = 3$, HL'

Experimental Section

Preparation. The method of Ablov, *et al.*, was used to synthesize $CuL(ClO_4)(H_2O)$.[1] Dark green prismatic crystals were obtained by recrystallization from methanol. *Anal.* Calcd for $Cu(C_6H_{11}N_2O_2)(ClO_4)(H_2O)$: C, 22.23; H, 4.04; N, 8.64. Found: C, 22.02; H, 3.69; N, 8.54.

By employing the same method and substituting 3-amino-1-propanol for 2-aminoethanol, dark green crystals of $CuL'(ClO_4)(H_2O)$ were obtained. *Anal.* Calcd for $Cu(C_7H_{13}N_2O_2)(H_2O)$: C, 24.86; H, 4.47; N, 8.28; Cl, 10.48. Found: C, 25.05; H, 4.20; N, 8.44; Cl, 10.59.

Magnetic Studies. The Faraday method was used to determine the magnetic susceptibility of $CuL(ClO_4)(H_2O)$ at 77, 195, and 298°K; $HgCo(NCS)_4$ was used as a calibrant and a diamagnetic correction of 128×10^{-6} cgsu per formula unit was derived from tabulated values.[3] The resulting susceptibilities per formula unit, 64×10^{-6}, 54×10^{-6}, and 28×10^{-6} cgsu at 77, 195, and 298°K, respectively, are of the magnitude of the temperature-independent paramagnetism of copper(II).

The magnetic susceptibility of $CuL'(ClO_4)(H_2O)$ was determined in the same way; values of 34×10^{-6} and 51×10^{-6} cgsu were obtained at 77 and 298°K, respectively.

Crystallographic Data Collection. Precession photographs of the $h0l$, $h1l$, $0kl$, and hkk reciprocal lattice levels and the full diffractometer data set (*vide infra*) revealed Laue symmetry $2/m$ and the systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), uniquely defining the space group as C_{2h}^5-$P2_1/c$ (No. 14).[4] For data collection a well-formed, multifaceted crystal was mounted collinear with the ($0kk$) row of the reciprocal lattice on a glass fiber attached to a goniometer head. The crystal was placed on a Picker automated four-circle diffractometer and 14 medium-intensity reflections at a variety of 2θ values were accurately centered using Zr-filtered Mo

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