Inorg. Chem. **1997,** *36,* 743−745

A Trinuclear Nickel(II) Complex Based on Bridging Oxalate and Cyanide Ligands

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Received July 22, 1996

Introduction

The design and synthesis of oxalato-bridged nickel(II) complexes have attracted much attention during the last few years due to the strong magneto-structural correlations found in these kinds of complexes.[1] In spite of these exhaustive studies, dimeric structures are predominant in the solid-state chemistry of μ-oxalato nickel(II) complexes[2] and only in the last three years infinitely extended networks based on transition metal oxalato complexes have been reported.[3] We report here the preparation, crystal structure, and magnetic properties of the compound $[\{Ni(dien)\}_2(\mu\text{-ox})\{\mu\text{-}Ni(CN)_4\}]$, which constitutes, as far we are aware, the first nickel(II) trimeric structure with an oxalato-bridging ligand. This work is a part of our research program on the chemistry of first-row transition metal oxalato complexes, which aims to analyze the influence of the peripheral ligands on the magnetic and structural properties of oxalato-bridged complexes. We have used the binuclear complex $[\{Ni(dien)H_2O\}_2(\mu\text{-ox})]Cl_2$[4] as a precursor owing to the lability of their water molecules which may be substituted by the pseudohalogen ligands, such as N_3^-, NCS^-, NCO^- and CN^-. When we have used cyanide, a neutral trinuclear complex has been obtained by replacing the two water molecules for two cyano groups belonging to a square-plane $[Ni(CN)_4]^{2-}$ unit.

Experimental Section

Synthesis. This compound was prepared via two different methods. Method A: To an aqueous solution (50 mL) of $[\{Ni(dien)H_2O\}_2(\mu\text{-ox})]Cl_2$ (1.00 g, 1.92 mmol) was added 0.25 g (3.82 mmol) of KCN. The mixture was refluxed for 10 min. A highly insoluble pink residue precipitates during the reaction. After filtration, the resulting blue solution was allowed to stand at room temperature for several days to give blue-purple prismatic single crystals of the complex, yield <10%. Method B: Two aqueous solutions of $K_2Ni(CN)_4$ (0.058 g, 0.24 mmol) and $[\{Ni(dien)H_2O\}_2(\mu\text{-ox})]Cl_2$ (0.25 g, 0.482 mmol) were mixed. The initially formed pink precipitate was removed by filtration, and the concentrated solution was allowed to cool slowly to room temperature to obtain single crystals of the compound, yield 15−20%. In both cases the crystals were collected, washed with cool water, and air dried. Anal. Calcd for $C_{14}H_{26}N_{10}Ni_3O_4$: C, 29.27; H, 4.56; N, 24.38. Found: C, 29.2; H, 4.30; N, 24.3. IR (KBr cm^{-1}): 2145 m, 2117 s (ν_{st}CN), 1637 vs, 1606 s (ν_{st}ox).

Table 1. Crystallographic Data for $[\{Ni(dien)\}_2(\mu\text{-ox})\{\mu\text{-}Ni(CN)_4\}]$

formula	$C_{14}H_{26}N_{10}Ni_3O_4$	space group	$I2/a$ (No. 15)
a, Å	13.133(1)	T, K	295
b, Å	11.644(1)	λ, Å	0.710 69
c, Å	14.154(1)	ρ_{obs}, ρ_{calc}, g cm^{-3}	1.77(3), 1.777
β, deg	97.13(1)	μ (Mo Kα), cm^{-1}	26.5
V, Å^3	2147.7(5)	R^a	0.027
Z	4	$R_w{}^a$	0.031
fw	574.51		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$.

Crystallographic Data Collection and Structure Determination. A blue-purple single crystal of the compound $[\{Ni(dien)\}_2(\mu\text{-ox})\{\mu\text{-}Ni(CN)_4\}]$ of dimensions $0.20 \times 0.28 \times 0.34$ mm^3 was mounted on an ENRAF-NONIUS CAD4 four-circle diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 69 Å) was used to collect the data. The lattice parameters were obtained at 296 K by least-squares fit of 25 well-centered independent reflexions in the range $10° < \theta < 14°$. The experimental density was determined by flotation method in a bromoform/carbon tetrachloride mixture. Details on crystal data are summarized in Table 1. Two standard reflexions were collected every 1 h as a monitor for crystal deterioration and/or misalignment, neither of which was observed. The data were corrected for Lorentz-polarization effects, but not for absorption. The scattering factors for neutral non-hydrogen atoms were corrected for both the real and the imaginary components of the anomalous dispersion.[5] A total of 3120 independent reflexions were measured in the range $1° < \theta < 30°$; 2387 were considered as observed with the selection criterium $I \geq 3\sigma(I)$.

The structure was solved by direct methods (DIRDIF 92)[6] and refined with the XRAY76.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier synthesis and refined isotropically. The final refinement leads to a convergence at $R = 0.027$ and $R_w = 0.031$. Final atomic coordinates are displayed in Table 2, while selected interatomic distances, angles, and hydrogen contacts are given in Table 3.

Physical Measurements. IR spectum was taken on a Nicolet 740 FTIR spectrophotometer in the 4000−400 cm^{-1} region as KBr pellets. The magnetic susceptibility was measured in the temperature range 4−300 K with a fully automated AZTEC DSM8 pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Bruker BE15 electromagnet operating at 1.8 T. Mercury(II) tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Correction for the diamagnetim of the trinuclear complex was estimated from the Pascal constant as -277×10^{-6} cm^3 mol^{-1}. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism (-100×10^{-6} cm^3 mol^{-1} per Ni(II)).

Results and Discussion

Synthesis and Spectroscopic Characterization. The preparation of the compound by using as a starting material KCN or $K_2[Ni(CN)_4]$ probably is a consequence of the high stability of the $[Ni(CN)_4]^{2-}$ complex ($\log \beta_4 = 31.3$)[8] , which leads to the initial formation of tetracyanonickelate(II) anion when the

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S0020-1669(96)00874-9 CCC: $14.00

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [{Ni(dien)}$_2$(μ-ox){μ-Ni(CN)$_4$}]

atom	*x*	*y*	*z*	U_{eq}[a]
Ni(1)	0.091 44(2)	0.206 33(2)	0.363 18(2)	19(0)
Ni(2)	0.250 00	0.570 88(3)	0.500 00	21(0)
O(1)	0.118 52(10)	0.174 15(14)	0.509 23(9)	25(0)
O(2)	0.248 39(10)	0.170 75(14)	0.376 28(9)	24(0)
C(1)	0.212 28(13)	0.173 42(16)	0.538 21(12)	19(0)
N(1)	−0.065 47(14)	0.219 71(17)	0.374 86(15)	31(1)
C(2)	−0.099 31(19)	0.102 78(22)	0.394 47(18)	36(1)
C(3)	−0.057 94(21)	0.022 57(24)	0.325 36(20)	40(1)
N(4)	0.055 05(14)	0.034 22(15)	0.333 11(12)	27(0)
C(5)	0.098 68(19)	0.006 40(20)	0.244 69(16)	33(1)
C(6)	0.073 30(18)	0.100 14(21)	0.171 86(14)	32(1)
N(7)	0.084 11(14)	0.215 29(16)	0.216 24(12)	26(0)
N(8)	0.131 86(14)	0.378 64(16)	0.393 14(13)	29(0)
C(9)	0.176 06(15)	0.454 52(16)	0.429 84(14)	25(0)
C(10)	0.316 55(17)	0.686 33(18)	0.576 65(17)	31(1)
N(11)	0.354 23(19)	0.758 62(22)	0.623 61(21)	51(1)

[a] $U_{eq} = {}^1/_3) \sum[\mathbf{U}_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cdot \cos(a_i, a_j)] \times 10^3$.

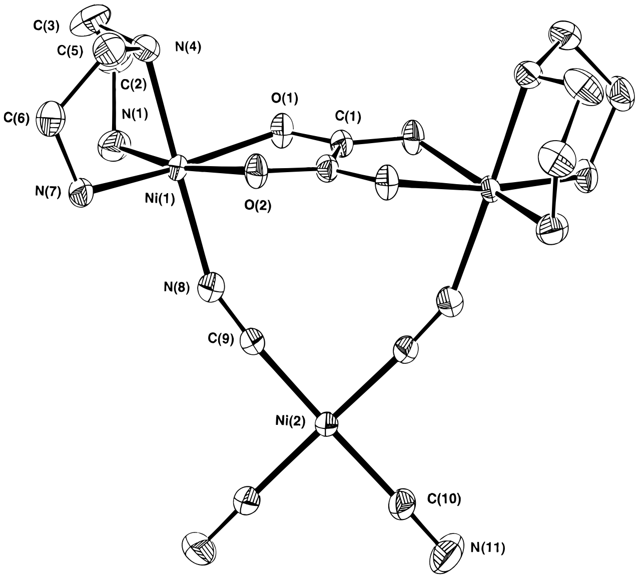

Figure 1. The structure of the [{Ni(dien)}$_2$(μ-ox){μ-Ni(CN)$_4$}]. Ellipsoids are drawn to encompass 50% electron density.

cyanide salt is added. This anion acts as a template for the formation of the trinuclear unit. The employing of another pseudohalogen species (X = N_3^-, NCO^-, and NCS^-) only produces a substitution of the water molecules by the corresponding pseudohalogen and dimer complexes of formula [{Ni(X)(dien)}$_2$(μ-ox)], which are obtained with the X ligand in a *trans* fashion with respect to the oxalate plane.[9] The IR spectrum of the compound exhibits, together with the bands of the bis(bidentate) oxalate ligand, two bands at 2145 and 2117 cm^{-1}, which are attributable to the ν_{st}(CN) in agreement with the presence of two different coordination modes (monodentate and bridging) of the cyanide ligand.

Description of the Structure. The X-ray crystal structure reveals the presence of a neutral trinuclear complex with a near C_{2v} symmetry (C_2 crystallographic symmetry), being the Ni(2) atom placed in a 2-fold axis which is perpendicular to the C(1)−C(1′) bond of the oxalate ligand (Figure 1). Two kinds of nonequivalent nickel atoms are present in the trimer, two nickel atoms Ni(1), with octahedral coordination, and Ni(2), with a square-plane coordination. The oxalate ligand is coordinated in bis(bidentate) fashion to the 2-fold axis related Ni(1) atoms. The sphere of coordination of each Ni(1) atom is completed by three nitrogen atoms from a diethylenetriamine ligand in *fac* arrangement and one nitrogen atom from a bridging cyanide ligand, which belongs to the square-plane coordination of Ni(2) atom (Figure 1). Thus, the $Ni(CN)_4^{2-}$ group acts as a *cis* bidentate-bridging unit between both octahedrically coordinated nickel atoms. The bridging *cis* coordination of the tetracyanonickelate(II) anion is very unusual and it has been recently reported in the polymeric compound $[(DMF)_{10}Yb_2\{Ni(CN)_4\}_3]_\infty$,[10] which contains both *trans* and *cis* coordinated $[Ni(CN)_4]^{2-}$ units. In our case, this *cis* disposition implies the rupture, during the synthesis process, of the starting binuclear complex in which the two water molecules were in *trans* disposition with respect to the oxalate plane. The *cis* coordination of $Ni(CN)_4^{2-}$ group also induces a significant distortion around octahedral Ni centers, forcing to the Ni−oxalato−Ni fragment to adopt a boat conformation[3a] and leading to a Ni−Ni distance between octahedral centers of 5.324 Å, which is the shortest one reported for this fragment in similar complexes.[2−4] The Ni(1) atoms are placed at 0.391 Å out of the oxalate mean-plane. The dihedral angle between the oxalate plane and the equatorial coordination Ni(1) plane is 10.3° with the Ni atoms displaced 0.11 Å toward the cyano-bridging ligand. The Ni−Ni distance between the octahedral and the square-plane centers is 5.010 Å, which is within the range found for similar compounds containing Ni−CN−Ni groups.[11]

Magnetic Properties. Although the title compound shows three d^8 Ni(II) ions, the substantially flat square-planar coordination of the $[Ni(CN)_4]^{2-}$ diamagnetic unit permits that, from a magnetic point of view, the compound can be treated as a dimeric complex in which the two octahedrically coordinated d^8 Ni(II) ions are linked by two different bridging ligands. The magnetic coupling between the two Ni(II) atoms might produce through both bridges, but the length of the exchange pathway through the bidentate tetracyanonickelate(II) ligand is large enough to predict that the magnetic interaction may take place mainly through the bischelating oxalate ligand, which is known to be very effective in mediating antiferromagnetic coupling between first-row transition metal ions separated by around 5.5 Å in homo-[2,3a,12] and heteropolynuclear compounds.[13] The thermal dependence of the molar magnetic susceptibility, χ_M, of the complexes (Figure 2) is characteristic of an antiferromagnetic interaction between the two single ion triplet states: the value of χ_M at room temperature is in the range expected for two $S = 1$ states ($\mu_{eff} = 4.12\ \mu_B$), increases as the temperature is lowered until a maximum is reached at 46 K, and finally decreases very quickly.

The ground state of a nickel(II) ion in an octahedral environment is orbitally nondegenerate, and as such it is possible

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Table 3. Selected Bond Distances (Å) and Angles (deg) for [{Ni(dien)}$_2$(μ-ox){μ-Ni(CN)$_4$}]

Ni(1) Coordination Sphere

	Ni(1)	O(1)	O(2)	N(1)	N(4)	N(7)	N(8)
O(1)	2.088(2)		2.692(2)	2.932(2)	3.008(2)		2.911(2)
O(2)	2.008(1)	80.3(1)			2.994(2)	2.974(2)	2.890(2)
N(1)	2.094(2)	89.1(1)	168.1(1)		2.784(3)	3.162(3)	3.169(3)
N(4)	2.092(2)	92.1(1)	91.5(1)	83.4(1)		2.736(3)	
N(7)	2.073(2)	169.6(1)	91.2(1)	98.7(1)	82.1(1)		3.145(3)
N(8)	2.105(2)	87.9(1)	87.1(1)	98.0(1)	178.6(1)	97.7(1)	

Ni(2) Coordination Plane

	Ni(2)	C(9)	C(10)	C(9)^a	C(10)^a
C(9)	1.878(2)			2.600(3)	2.703(3)
C(10)	1.874(2)	175.7(1)			2.612(3)
C(9)^a	1.878(2)	87.6(1)	98.2(9)		
C(10)^a	1.874(2)	92.2(1)	88.3(1)	175.7(1)	

Ligands

Oxalate			
C(1)−O(1)	1.249(2)	O(1)−C(1)−C(1)^a	117.3(2)
C(1)^a−O(2)	1.256(2)	O(2)−C(1)^a−C(1)	116.7(2)
C(1)−C(1)^a	1.555(2)	C(1)−O(1)−Ni(1)	111.5(1)
		C(1)^a−O(2)−Ni(1)	111.3(1)
Diethylenetriamine			
N(1)−C(2)	1.469(3)	N(1)−C(2)−C(3)	108.1(2)
C(2)−C(3)	1.502(4)	C(2)−C(3)−N(4)	109.6(2)
C(3)−N(4)	1.480(3)	C(3)−N(4)−C(5)	114.1(2)
N(4)−C(5)	1.510(3)	N(4)−C(5)−C(6)	110.2(2)
C(5)−C(6)	1.480(3)	C(5)−C(6)−N(7)	111.3(2)
C(6)−N(7)	1.476(3)		
Cyanide			
C(9)−N(8)	1.146(3)	Ni(1)−N(8)−C(9)	158.0(2)
C(10)−N(11)	1.146(3)	Ni(2)−C(9)−N(8)	174.9(2)
		Ni(2)−C(10)−N(11)	177.8(2)

Hydrogen Bonds

D−H···A	D···A	D−H	H···A	D−H···A
N(7)−H(71)···O(2)^b	3.005(2)	0.83(4)	2.22(4)	158(4)
N(7)−H(72)···N(11)^c	3.062(3)	0.85(4)	2.47(4)	141(3)

^{a} $^1/_2 - x, y, 1 - z$. ^{b} $^1/_2 - x, ^1/_2 - y, ^1/_2 - z$. ^{c} $-^1/_2 + x, -^1/_2 + y, -^1/_2 + z$.

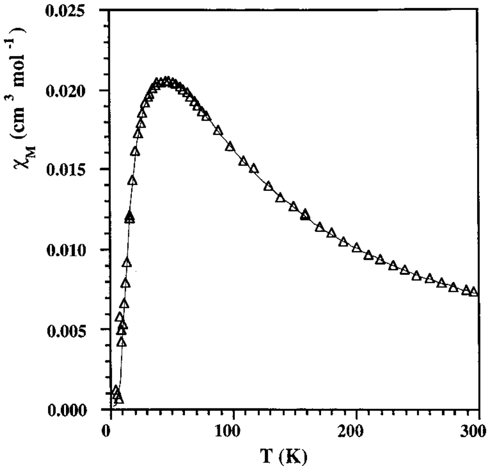

Figure 2. Thermal dependence of the molar magnetic susceptibility for [{Ni(dien)}$_2$(μ-ox){μ-Ni(CN)$_4$}].

to represent the intradimer magnetic interaction, J, with the isotropic spin hamiltonian $H = -JS_A \cdot S_B$. The molar magnetic susceptibility for a nickel(II) dimer (local spins $S_A = S_B = 1$) may be expressed by eq 1,

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \frac{\exp(J/kT) + 5\exp(3J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT)} \quad (1)$$

where N, β, K, g, and T have their usual meanings and it is assumed that $g_x = g_y = g_z = g$. Although, nickel(II) in axial symmetry can have a large zero−field splitting, D, the magnetic behavior of nickel(II) dimers closely follows eq 1 when a relatively strong antiferromagnetic interaction is operative ($|J| \geq 20$ cm^{-1}).[14] If the antiferromagnetic coupling is weak or the coupling is ferromagnetic, the influence of D must be taken into account to describe the magnetic behavior at low temperatures.[14] The occurrence of a relatively large intradimer antiferromagnetic coupling in this complex makes unnecessary the consideration of D, and a good fit of the experimental data to eq 1 is obtained. The best−fit parameters obtained from the compound by minimizing the R factor $\sum(\chi_M^{obs} - \chi_M^{calc})^2/\sum(\chi_M^{obs})^2$ were $J = -31.2$ cm^{-1}, $g = 2.15$, and $R = 2.5 \times 10^{-5}$. The value of the exchange coupling is slightly lower than those reported for oxalato−bridged nickel(II) dimers ($32 < -J < 39$ cm^{-1})[4] in which the nickel atoms are placed in a NiN$_4$O$_2$ environment. This fact is due to the above-mentioned strong deviation from the planarity of the Ni−ox−Ni fragment in the compound.

Acknowledgment. This work was supported by UPV/EHU (Grant 169-310-EA134/95).

Supporting Information Available: Tables of crystallographic data, final fractional coordinates for all atoms, bond lengths, bond angles, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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