Studies on Mixed Chelates. XXI. Synthesis and Crystal Structure of the Binuclear Nickel(II) Complex, μ-(Oxalato)bis[(acetylacetonato)(*N,N,N′,N′*-tetramethylethylenediamine)nickel(II)]

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Synopsis. A new binuclear nickel(II) complex having the formula $[Ni_2(acac)_2(tmen)_2ox]$ (acac = acetylacetonate, tmen = *N,N,N′,N′*-tetramethylethylenediamine, ox = oxalate) has been characterized, and its crystal structure has been determined at room temperature. This crystal was obtained in its solvated form, $[Ni_2(acac)_2(tmen)_2ox]\cdot 2TCE$ (where TCE = 1,1,2,2-tetrachroloethane); orthorhombic system, space group *Pcab* (No. 61), with $a = 20.172(4)$, $b = 17.180(5)$, $c = 13.132(3)$ Å, $Z = 4$, $R = 0.044$. The oxalate ligand acts as a bridging group between the two Ni(II) moieties.

Some chromotropic mononuclear nickel(II) mixed ligand complexes in this series, [Ni(dike)(diam)]X, where dike is the β-diketonate ion, diam the *N*-alkylated ethylenediamine, and X the non-coordinating anion, such as ClO_4^-, BPh_4^-,[1—5] can act as a Lewis acid, since they are four-coordinate square-planar chelates and the ligand field strength in these complexes are rather weak, i.e., coordination unsaturation. It is, therefore, easy for the chelate cation, $[Ni(dike)(diam)]^+$, to form a dinuclear complex with a bridging ligand, such as an oxalate ion. In the present work, we obtained the dinuclear Ni(II) mixed complex, [(tmen)(acac)Ni(ox)Ni(acac)(tmen)]; some of the properties of the complex, i.e., its crystal structure as well as spectral and magnetic behaviors, are reported.

Experimental

Synthesis of the Complex, $[Ni_2(acac)_2(tmen)_2(ox)]$. [Ni(acac)(tmen)]$BPh_4$ was synthesized according to a reported method.[3] This complex was dissolved in a CH_3CN/MeOH (1 : 1 v/v) mixture; to this solution a saturated aqueous solution of $K_2C_2O_4$ was added. After filtration, a blue solution was dried up and the residue was dissolved into 1,2-dichloroethane to give a pale-blue powder without any solvent molecule of crystallization. Analytical data: Found: C, 45.08; H, 7.07; N, 8.73%. Calcd for $Ni_2C_{24}H_{46}N_4O_8$: C, 45.32; H, 7.29; N, 8.81%. This unsolvated complex was used for all of the measurements in this work, except for the X-ray analytical study. For the crystal-structure determination, the powdered compound was dissolved into 1,1,2,2-tetrachloroethane (TCE) to give fine blue crystals containing two TCE molecules of crystallization.

Physical Measurements. IR and electronic spectral measurements of the complex were the same as those reported before.[2—5] The magnetic susceptibilities at room temperature were determined using the Gouy method; measurements over the range from liquid-helium temperature to room temperature were carried out using a Faraday apparatus designed by one of us (W.M.), and calibrated by $CuSO_4\cdot 5H_2O$.[6,7]

The IR data of this complex show the characteristic bands of the oxalate bridging ligand.[8] Three peaks (ν_{asym}(O–C–O), ν_{sym}(O–C–O), and δ(O–C–O)) of oxalate are found at 1647, 1312, and 799 cm^{-1}, respectively, which are comparable with those of $[Ni_2(L)_2ox]^{2+}$ previously reported;[9—11] L is a tetradentate ligand. The ν(C=C) and ν(C=O) bands of the acetylacetonate ion are found at 1598, 1515 cm^{-1}, respectively, which are comparable with those of an octahedrally coordinated nickel(II) complex, such as [Ni(tmen)(acac)$(H_2O)_2$](ClO_4).[3]

Crystal Structure Analysis of $[Ni_2(acac)_2(tmen)_2ox]\cdot 2TCE$. Blue rectangular-parallelpiped crystals were grown from a 1,1,2,2-tetrachloroethane solution. A crystal of approximate dimension (0.40×0.40×0.35 mm) was used. Accurate cell parameters were determined by a least-squares fit for 25 reflections within the range $25° > 2\theta > 30°$ measured on a Rigaku AFC-5 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromated by graphite. Crystal data: f.w. = 971.8, $[Ni_2N_4O_8C_{24}H_{46}][C_4H_4Cl_8]$ orthorombic, *Pcab* (No. 61), $a = 20.172(4)$, $b = 17.180(5)$, $c = 13.132(3)$ Å, $V = 4551(2)$ Å^3, $Z = 4$, $d_c = 1.418$ g cm^{-3}, $\mu = 13.5$ cm^{-1}, $F(000) = 2008$.

Reflection data were collected in the 2θ–ω scan mode up to $2\theta = 45°$ with scan widths of $\Delta\omega = (1.1 + 0.45\tan\theta)°$. The backgrounds were counted for 6s at both ends of the scan. Three standard reflections were recorded after every 100 reflections. No significant intensity change was observed. A total of 2207 reflections were collected at a rate of 3°(2θ) min^{-1}, of which 1173 were treated as being significant ($|F_o| > 3\sigma(|F_o|)$). The structure was solved by a direct method using the program MULTAN,[12] and was refined by block-diagonal least squares with the UNICS III Package.[13] The minimized quantity was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography Vol. IV.[14] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms found in difference Fourier maps and checked by geometrical calculations (C–H, 1.0 Å) were refined isotropically. The max and min peaks in the final difference map were 0.9 and −0.8 eÅ^3.

Max shift/error in final cycle of non-hydrogen atom, Δ/σ, is 1.2 in Z of C6. Final R (and R_w) was 0.044 (0.055).[15] Computations were carried out on a HITAC M-680 computer at the IMS Computer Center.

Results and Discussion

The structure of this complex comprises of two 1,1,2, 2-tetrachloroethane (TCE) molecules of crystallization, and a binuclear complex unit having a symmetry center at the midpoint of the C(12)–C(12′) bond $(1-x, 1-y, 1-z)$ of the oxalate bridge. The molecular geometry and the atom labelling scheme for the molecule are shown in Fig. 1. The final positional parameters ($\times 10^{-4}$) and equivalent isotropic temperature factors are given in Table 1. The nickel coordination geometry is octahedral with two nitrogen atoms from tmen, and four oxygen atoms from acac and the oxalate briging ligand. The oxalate ion joins two adjacent nickel(II) ions by its oxygen atoms occupying two cis positions. From the viewpoint of the formation of mixed ligand complexes, the complex in this study is an interesting example of Ni(II) mixed chelates [Ni(A)(B)(C)] containing three different bidentate ligands (quarternary system), such as acac, tmen, and the bridging oxalate. There are not many examples of quarternary complexes, since the Ni(II) ion is a labile metal ion, and easily tends to cause a rearrangment of the ligand (changing to binary or ternary systems). The nickel–nickel separation within the binuclear unit is 5.36 Å. The bond distances and angles involving non-hydrogen atoms are listed in Table 2. Two Ni–N (tmen) bonds (2.143(7), 2.116(7) Å) and the two Ni–O (acac) bonds (1.991(6), 2.000(6) Å) are comparable with the values found in [Ni(acac)(tmen)(CH_3OH)(H_2O)]ClO_4, which were 2.157(6), 2.131(6) Å and 2.032(4), 1.989(5) Å, respectively.[16] The Ni–O (oxalate) bonds (2.067(5) and 2.073(5) Å) range over the area within 2.069—2.111 Å observed in other binuclear complexes with the μ-oxalato bridge, $[Ni_2(L)_2ox]^{2+}$. The slight distortion of the octahedron is apparently observed from the angles around nickel:

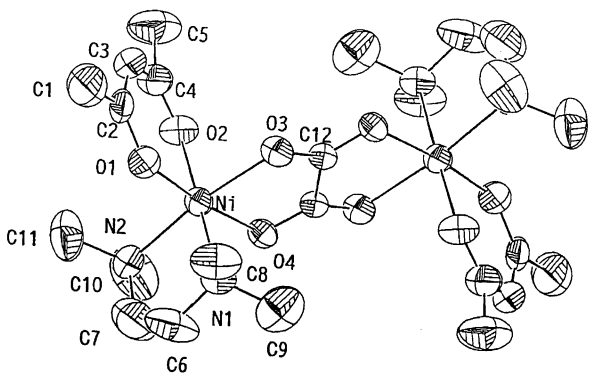

Fig. 1. Molecular structure of the complex $[Ni_2(acac)_2(tmen)_2ox]\cdot 2TCE$ along with the atom numbering scheme. The hydrogen atoms and two TCE molecules are not shown for the sake of clarity.

Table 1. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors (Hamilton, 1959)

Atom	x	y	z	B_{eq}/Å^2
Ni1	5265(1)	5453(1)	3089(1)	3.9
Cl1	2903(2)	7205(2)	5942(3)	11.4
Cl2	4086(2)	7686(2)	4707(3)	10.8
Cl3	2819(1)	5729(2)	4600(3)	9.9
Cl4	2816(2)	7228(2)	3457(2)	10.5
O1	4876(3)	6254(3)	2169(4)	5.6
O2	4532(2)	4720(3)	2723(5)	6.0
O3	4713(3)	5807(3)	4333(4)	4.4
O4	5574(2)	4630(3)	4141(4)	4.1
N1	6063(3)	6229(4)	3451(5)	4.7
N2	5922(3)	5018(4)	1969(5)	5.2
C1	4096(6)	6959(7)	1204(9)	10.4
C2	4300(4)	6242(6)	1776(6)	6.1
C3	3846(4)	5639(6)	1893(7)	6.9
C4	4012(4)	4912(6)	2303(7)	6.5
C5	3463(5)	4341(7)	2266(10)	10.5
C6	6559(5)	6043(6)	2708(10)	9.8
C7	6513(5)	5454(8)	2100(9)	11.4
C8	5882(5)	7039(6)	3398(9)	8.2
C9	6350(6)	6118(6)	4456(9)	9.2
C10	5671(6)	5127(6)	953(8)	9.1
C11	6040(6)	4192(6)	2068(9)	10.1
C12	4748(4)	5339(4)	5059(6)	3.2
C13	3486(6)	6823(7)	5081(8)	11.3
C14	3350(6)	6655(8)	4169(8)	11.0

the five-membered chelate rings, such as the N(1)–Ni–N(2) (Ni-tmen) and O(3)–Ni–O(4) (ox), observed as 84.4(2)° and 80.5(2)°, respectively, are smaller than that of the six-membered ring (Ni-acac 89.9(2)°). The chelate ring formed by the acetylacetonate ligand and a Ni(II) ion is nearly in the same plane, and the intraligand bond lengths of acac are not different from those of the mononuclear complex [Ni(acac)(tmen)(CH_3OH)-(H_2O)]ClO_4. The bond length of C(6)–C(7) of the ethylenediamine moiety (in tmen) is abnormally short as the normal C–C single bond, which results in a disorder of the ethylene moiety in the tmen ligand due to a large observed thermal ellipsoid.

The absorption spectra of this complex have been measured in both the solid state and a 1,2-dichroloethane (DCE) solution. The color of TCE solvated crystals is quite similar to that of the non-solvated powder complex. Two spin-allowed d–d transitions from $^3A_{2g}$ to $^3T_{2g}$ and $^3T_{1g}$(F) are observed at 9.7 and 16.4 ($\times 10^3$ cm^{-1}), respectively, in the reflectance spectra and at 9.6 and 16.3 ($\times 10^3$ cm^{-1}) in the DCE solution, as expected for a d^8 configuration in a octahedral ligand field.

Figure 2 shows magnetic susceptibility data, (χ_A) in the temperature range from 4.2 to 300 K. The susceptibility values for this compound have a peak at 42 K. This means that there is an intramolecular antiferromagnetic interaction between two Ni(II) ions. When the electronic ground state of nickel(II) com-

Table 2. Bond Distances (Å) and Angles (°) for $[Ni_2(acac)_2(tmen)_2ox]\cdot 2TCE$

Nickel environment			
Ni–O(1)	1.991(6)	Ni–O(2)	2.000(6)
Ni–O(3)	2.067(5)	Ni–O(4)	2.073(5)
Ni–N(1)	2.143(7)	Ni–N(2)	2.116(7)
O(1)–Ni–O(2)	89.9(2)	O(1)–Ni–O(3)	93.7(2)
O(1)–Ni–O(4)	173.6(2)	O(1)–Ni–N(1)	90.0(2)
O(1)–Ni–N(2)	93.9(2)	O(2)–Ni–O(3)	88.6(2)
O(2)–Ni–O(4)	87.2(2)	O(2)–Ni–N(1)	178.6(2)
O(2)–Ni–N(2)	94.2(2)	O(3)–Ni–O(4)	80.5(2)
O(3)–Ni–N(1)	92.6(2)	O(3)–Ni–N(2)	171.7(2)
O(4)–Ni–N(1)	92.8(2)	O(4)–Ni–N(2)	91.1(2)
N(1)–Ni–N(2)	84.4(2)		
N,N,N′,N′–Tetramethylethylenediamine ligand			
N(1)–C(6)	1.43(1)	N(1)–C(8)	1.44(1)
N(1)–C(9)	1.45(1)	N(2)–C(7)	1.41(1)
N(2)–C(10)	1.43(1)	N(2)–C(11)	1.44(1)
C(6)–C(7)	1.29(1)		
Ni–N(1)–C(6)	103.6(6)	Ni–N(1)–C(8)	113.4(6)
Ni–N(1)–C(9)	114.7(6)	C(6)–N(1)–C(8)	111.0(8)
C(6)–N(1)–C(9)	108.1(8)	C(8)–N(1)–C(9)	105.7(8)
Ni–N(2)–C(7)	104.8(6)	Ni–N(2)–C(10)	112.2(6)
Ni–N(2)–C(11)	112.8(6)	C(7)–N(2)–C(10)	109.7(8)
C(7)–N(2)–C(11)	111.6(8)		
Acetylacetonate ligand			
O(1)–C(2)	1.27(1)	C(1)–C(2)	1.50(1)
C(2)–C(3)	1.38(1)	C(3)–C(4)	1.40(1)
C(4)–C(5)	1.48(1)	O(2)–C(4)	1.22(1)
Ni–O(1)–C(2)	126.4(6)	Ni–O(2)–C(4)	124.6(6)
O(1)–C(2)–C(1)	116.0(8)	O(1)–C(2)–C(3)	124.7(8)
C(1)–C(2)–C(3)	119.1(8)	C(2)–C(3)–C(4)	123.3(8)
Oxalate bridge			
O(3)–C(12)	1.249(8)	O(4′)–C(12)	1.234(9)
C(12)–C(12′)	1.55(1)		

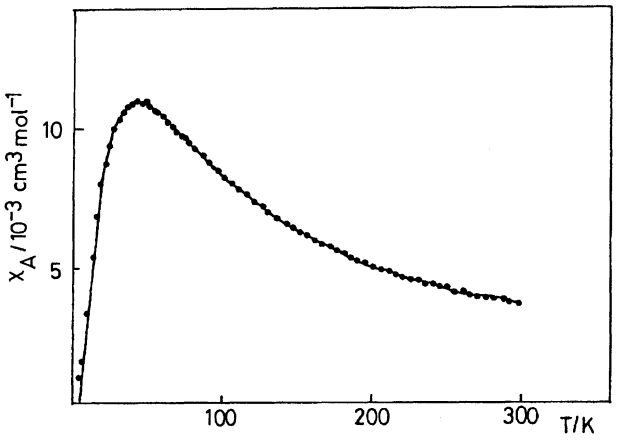

Fig. 2. Plots of the magnetic susceptibility vs. temperature for $[Ni_2(acac)_2(tmen)_2ox]$.

plexes under an octahedral symmetry is not degenerate ($^3A_{1g}$), the intramolecular exchange interactions are expressed by the following isotropic spin-Hamiltonian $H=-2JS_A\cdot S_B$, where J means an exchange integral and the respective Ni(II) spin states are $S_A=1$. $S_B=1$. The data were fitted to Eq. 1 where N, β, K, and g have usual meanings.

$$\chi = \frac{Ng^2\beta^2}{kT}\left[\frac{5+\exp(-4J/kT)}{5+3\exp(-4J/kT)+\exp(-6J/kT)}\right] \quad (1)$$

A theoretical curve of Eq. 1 is shown in this figure as a solid line. This fitting leads to the values, $J=-14.3$ cm^{-1}, which is a bit smaller values, but not greatly deviated from those reported for the μ-oxalato Ni(II) binuclear complexes ($J=-25.5$——-39 cm^{-1} where $H=-JS_A\cdot S_B$),[9—11,17—19] and $g=2.18$. The data obtained in this case show that the main factor influencing the strength of the antiferromagnetic coupling is the extent of overlap between the magnetic orbitals of the para-

magnetic metal ions and those of the μ-oxalato bridging ligand. In other words, there is no influence of the change in the remaining terminal ligands to the magnetic interaction between the two metal ions, although in this case these ligands are very bulky and might hinder the intermolecular magnetic interactions.[20]

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