Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science, Calcutta 700 032, India

A Tris(thioxanthate) of Nickel(II) and Its Transformation to a Dinuclear Trithiocarbonate Complex. Synthesis and Structure of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$

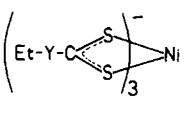
Suranjan Bhanja Choudhury and Animesh Chakravorty*

Received July 30, 1991

The tris(thioxanthate)nickel(II) salt $[Et_4N][Ni(txn)_3]$ has been synthesized. The S_6-coordinated bivalent metal center (2.97 μ_B) is oxidizable, the $E_{1/2}$ of the $Ni^{III}(txn)_3$–$Ni^{II}(txn)_3^-$ couple being 0.09 V vs SCE (CH_2Cl_2, 253 K). The frozen-solution (77 K) EPR spectrum of electrogenerated $Ni(txn)_3$ is compatible with the $d_{z^2}{}^1$ ground state ($g_\parallel$, 2.083; $g_\perp$ components, 2.122 and 2.146). At ambient temperature $Ni(txn)_3^-$ undergoes a facile spontaneous decomposition, affording the dimeric complex $Ni_2(SEt)_2(CS_3)_2^{2-}$. A rationale for this transformation is proposed. The structure of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ is reported: a = 31.279 (9) Å, b = 13.670 (5) Å, c = 16.900 (4) Å, β = 102.63 (2)°, V = 7050 (4) Å^3, R = 0.0733, R_w = 0.0720, space group $C2/c$, and Z = 8. In the dimeric anion, the metal atoms are thiolato bridged and one CS_3^{2-} ligand is chelated to each metal center. The average Ni–S(chelate) and Ni–S(bridge) lengths are 2.173 (6) and 2.189 (5) Å, respectively; the Ni···Ni contact (d) is 2.767 (3) Å. The dihedral angle (α) between the two edge-sharing NiS_4 planes is 111.1 (2)°. In a group of complexes having this structural feature, d correlates linearly with sin (α/2).

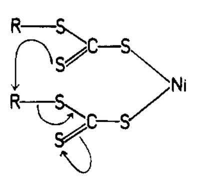
Introduction

As part of our program on the chemistry of sulfur-ligated nickel oxidation states, we recently described the tris xanthate, $Ni(xn)_3^-$ (**1**).[1] The hitherto unreported thioxanthate $Ni(txn)_3^-$ (**2**), has now been synthesized and characterized. Its spectral, magnetic, and electrochemical properties are expectedly similar to those of **1**. What makes **2** noteworthy is that, unlike **1**, it undergoes a facile and spontaneous transformation in solution affording the new dimer $Ni_2^{II}(SEt)_2(CS_3)_2^{2-}$, incorporating trithiocarbonate chelation. The X-ray structure of the dimer (Et_4N^+ salt) is reported and its probable mode of formation noted.



1, Y=O, $Ni(xn)_3^-$

2, Y=S, $Ni(txn)_3^-$



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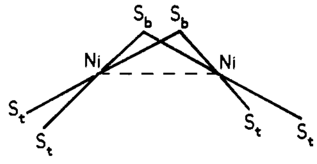

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Results and Discussion

A. The Tris(thioxanthate) Complex. a. Synthesis and Characterization. The diamagnetic bis(thioxanthate) chelate $Ni(txn)_2$ has been known for some years[2] but the tris chelate **2** has never been described. The brown paramagnetic (2.97 μ_B, S = 1) salt $[Et_4N][Ni(txn)_3]$ has been isolated in excellent yields by reacting potassium ethylthioxanthate with nickel(II) chloride hexahydrate in a 3:1 mole ratio in water in the presence of excess tetraethylammonium chloride. The use of water as the reaction medium is crucial for the synthesis—the trischelate salt is insoluble in this solvent and precipitates immediately. Solvents in which it is soluble to a significant extent (acetone, acetonitrile, ethanol) promote its decomposition and are unsuitable; vide infra. All solution measurements noted below were performed in dichloromethane solution at ≤273 K. In this environment the decomposition of the complex is relatively slow.

The 1:1 electrolytic complex (Λ = 144 Ω^{-1} cm^{-2} mol^{-1}) displays ligand field bands at 1075 nm (ϵ, 50 mol^{-1} cm^{-1}) and 1250 nm (ϵ, 30 mol^{-1} cm^{-1}) assigned to split components of the octahedral ν_1 transition (Figure 1). The electrode reaction of eq 1 is observable by cyclic voltammetry with $E_{1/2}$ = 0.09 V versus SCE. The one-electron

$$Ni^{III}(txn)_3 + e^- \rightleftharpoons Ni^{II}(txn)_3^- \qquad (1)$$

stoichiometry of the electrode reaction is confirmed by coulometric oxidation at 0.30V. When the electrooxidized solution is frozen (77 K), an axial EPR spectrum is observed with small rhombic splitting: $g_\parallel$, 2.083; $g_\perp$ components, 2.122 and 2.146. The spectrum is assigned to the nickel(III) complex $Ni(txn)_3$ (low-spin d^7). The $g_\perp > g_\parallel$ situation corresponds to the $d_{z^2}{}^1$ ground state. The voltammogram and EPR spectra are displayed in Figure 2.

The above-noted properties of the tris(thioxanthate) are similar to those of the xanthate congener.[1,3] It is logical to conclude that the thioxanthate also has the gross NiS_6 structure (**1** and **2**). Anionic NiS_6 species,[1,3,4] unlike cationic ones,[5] are rare.

b. Decomposition in Solution and Isolation of a Dinuclear Trithiocarbonate Complex. When $[Et_4N][Ni(txn)_3]$ is dissolved in acetone (acetonitrile or ethanol can be used with similar results), the original brown color rapidly changes, forming a greenish solution from which the dark-colored diamagnetic complex $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ can be isolated in good yield. It is stable in solution and acts as a 2:1 electrolyte (Λ = 257 Ω^{-1} cm^{-2} mol^{-1} in acetonitrile). Its characteristic absorption spectrum has strong bands in the visible region and is shown in Figure 1.

Transition metal trithiocarbonates constitute a small family.[6,7] The only well-characterized nickel(II) complex is the bis chelate $Ni(CS_3)_2^{2-}$ prepared by the reaction of preformed CS_3^{2-} with a nickel(II) salt.[8-10] To our knowledge there is no precedence of the formation of trithiocarbonates from thioxanthates in the coordination environment of a metal. In platinum metal chemistry there is an instance of dithiocarbonate formation from a tris-

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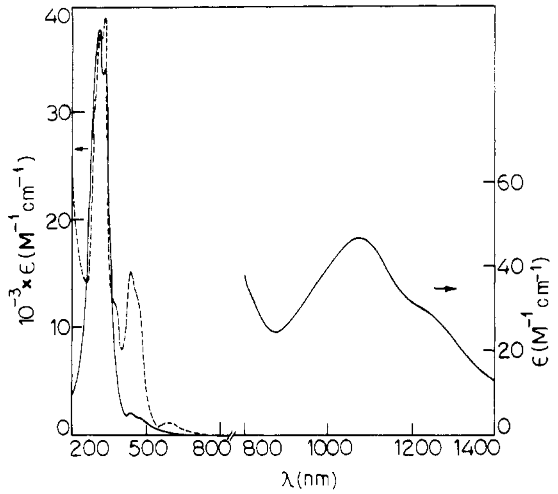

Figure 1. Electronic spectra of $[Et_4N][Ni(txn)_3]$ in dichloromethane at 273 K (—) and of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ in acetonitrile at 298 K (- -).

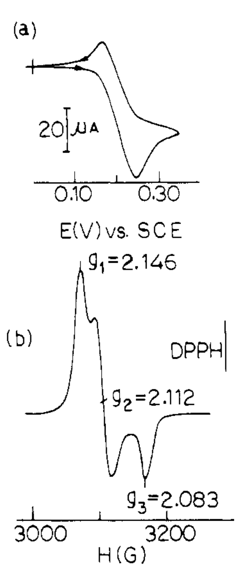

Figure 2. (a) Cyclic voltammogram (scan rate 50 mV s^{-1}) of a 10^{-3} M solution of $[Et_4N][Ni(txn)_3]$ in dichloromethane at 253 K at a platinum electrode. (b) X-Band (9.11 GHz) frozen-solution (77 K) EPR spectrum of electrogenerated $Ni(txn)_3$ in dichloromethane.

(xanthate).[11] By analogy the intermediate 3 is proposed for the present conversion. In 3 monodenticity of thioxanthates could arise via solvolysis (coordinated solvent and the third thioxanthate ligand are not shown). The electron movements shown in 3 afford a trithiocarbonate diester and a trithiocarbonate dianion—the latter can then chelate the metal, eliminating the ester from the coordination sphere.

Thiolato bridge formation does not raise any new questions—the reaction of eq 2 is well-documented[12] for homoleptic thioxanthates including $Ni(txn)_2$.[2] In summary, two of the txn ligands of $Ni(txn)_3^-$ give rise to trithiocarbonate and the third one affords thiolate.[13]

$$2M(RSCS_2)_p \rightarrow M_2(SR)_2(RSCS_2)_{2p-2} + 2CS_2 \qquad (2)$$

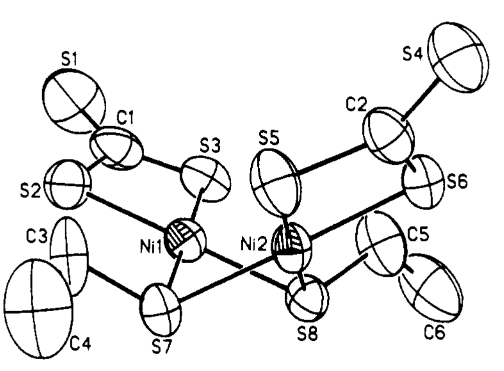

Figure 3. ORTEP plot of the anion of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ showing 20% thermal probability ellipsoids.

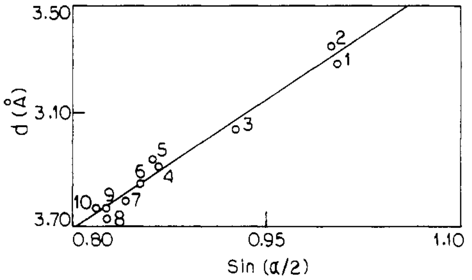

Figure 4. Linear plot of *d* versus sin (α/2): 1, $Ni_2(p\text{-}ClBzS)_6^{2-}$ (*d* = 3.273 Å; sin (α/2) = 1.000);[16] 2, $Ni_2(SEt)_6^{2-}$ (3.355 Å; 0.9999);[15] 3, $Ni_8(SCH_2COOEt)_{16}$ (3.050 Å; 0.9239);[23] 4, $[Ni(SEt)_2]_6$ (2.920 Å; 0.8660);[22] 5, $Ni_2(SCH_2CH_2S)_3^{2-}$ (2.9414 Å; 0.8619);[19] 6, $Ni_3(SCH_2CH_2S)_4^{2-}$ (2.856 Å; 0.8517);[14] 7, $Ni_2(SBz)_2(S_2CSBz)_2$ (2.795 Å; 0.8401);[18] 8, $Ni_2(SCH_2CH_2SCH_2CH_2S)_2$ (2.733 Å; 0.8256);[20] 9, $Ni_2(SEt)_2(CS_3)_2^{2-}$ (2.767 Å; 0.8246); 10, $Ni_2(SEt)_2(S_2CSEt)_2$ (2.763 Å; 0.8202).[17]

Table I. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$

	Distances		
Ni(1)···Ni(2)	2.767 (3)		
Ni(1)–S(2)	2.172 (6)	Ni(2)–S(5)	2.172 (4)
Ni(1)–S(3)	2.170 (5)	Ni(2)–S(6)	2.176 (4)
Ni(1)–S(7)	2.185 (4)	Ni(2)–S(7)	2.199 (4)
Ni(1)–S(8)	2.189 (5)	Ni(2)–S(8)	2.184 (4)
	Angles		
S(2)–Ni(1)–S(3)	78.3 (3)	S(5)–Ni(2)–S(6)	77.8 (2)
S(2)–Ni(1)–S(7)	101.1 (2)	S(5)–Ni(2)–S(7)	101.0 (2)
S(2)–Ni(1)–S(8)	178.0 (2)	S(5)–Ni(2)–S(8)	177.8 (2)
S(3)–Ni(1)–S(7)	179.1 (2)	S(6)–Ni(2)–S(7)	178.6 (2)
S(3)–Ni(1)–S(8)	100.0 (2)	S(6)–Ni(2)–S(8)	100.8 (2)
S(7)–Ni(1)–S(8)	80.6 (2)	S(7)–Ni(2)–S(8)	80.4 (2)

B. Structure of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$. A view of the dinuclear anion is displayed in Figure 3, and selected bond parameters are listed in Table I. The donor atoms in the dimer are distinguished below as follows: S_t, terminally chelated trithiocarbonate sulfur; S_u, uncoordinated trithiocarbonate sulfur; S_b, bridged thiolate sulfur.

Each metal atom is chelated by a trithiocarbonate dianion, forming a planar, four-membered NiS_2C ring. The bite angle lies close to 80°. Chelation imposes a large angular deviation from the possible threefold symmetry of the ligand. The S_t–C–S_t angle is constrained to ~106° while the average of two S_t–C–S_u angle is ~127°. Corresponding to this, the nonbonded S_t···S_t contact is considerably shorter than the S_t···S_u contact—averages being 2.737 (6) and 2.994 (5) Å, respectively. The average Ni–S_t distance is 2.173 (6) Å. In the bis chelate $Ni(CS_3)_2^{2-}$, the binding of the trithiocarbonate dianion is similar, the Ni–S_t distance being 2.20 (1) Å.[10]

The two $Ni(CS_3)$ moieties in the dinuclear anion are linked by two mercaptide bridges. The NiS_4 coordination environments are nearly perfectly planar. Indeed whole $Ni(CS_3)(S_b)_2$ fragments are almost perfectly planar with a mean deviation of ≤0.03 Å.

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[13] We have not been able to follow the time evolution of the reaction spectrophotometrically because of the invariable occurrence of an interfering side reaction leading to the deposition of a nonnitrogenous amorphous insoluble material. About 30% of the total nickel occurs in this solid and the remaining 70% finds its way into the soluble dimer (see Experimental Section).

The dihedral angle between the two planes of this type is 111.1 (2)°. The ethyl groups bonded to the wedge-shaped metal thiolate fragment, $Ni_2(S_b)_2$, span the syn–endo configuration (Figure 3). The Ni···Ni and S_b···S_b contacts are respectively 2.767 (3) and 2.828 (5) Å. The Ni–S_b distances average to 2.189 (5) Å, which is slightly longer than the Ni–S_t average.

Structural feature **4**, involving sharing of NiS_4 units via S_b, occurs in a number of systems.[14-23] For symmetrical bridging of planar NiS_4 moieties, $d = 2l \cos(\theta/2) \sin(\alpha/2)$ where l is the Ni–S_b distance, θ is the S_b–Ni–S_b angle, and α is the dihedral angle between the NiS_4 planes. In the different complexes[14-23] large variations occur in α (90–180°) and d (2.67–3.36 Å); l and θ also vary but within relatively small ranges. In the group of 10 species represented in Figure 4 the conditions of NiS_4 planarity and bridge symmetry are approximately obeyed and the range of the various quantities are as follows: $\alpha = 110–180°$, $d = 2.73–3.36$ Å, $l = 2.20 \pm 0.02$ Å, and $\theta = 82.4 \pm 2.4°$. A good linear correlation exists between d and $\sin(\alpha/2)$, as shown in Figure 4. The slope (3.11 Å) and intercept (0.21 Å) of the straight line evidently provide an effective cover for the deviations from NiS_4 planarity and bridge symmetry and for variations of l and θ. When the deviations/variations are large, the linear match will no doubt fail, but such species are rare. An example is $Ni_4(SC_5H_9NMe)_8$[21] in which $\alpha = 90°$ and $d = 2.665$ (5) Å. Here the nickel atoms lie 0.22 Å away from the S_4 plane. If each metal atom is hypothetically shifted to ensure NiS_4 planarity, the Ni···Ni contact works out to be 2.36 Å. The calculated d at $\alpha = 90°$ from Figure 4 is 2.40 Å.

C. Concluding Remarks. The main results of this research will be summarized. A tris(thioxanthate) of nickel(II) has been isolated, $[Et_4N][Ni(txn)_3]$. Its magnetic, spectral, and electrochemical properties are analogous to those of the corresponding xanthate (NiS_6 coordination). The electrogenerated oxidized complex $Ni^{III}(txn)_3$ having the $d_{z^2}{}^1$ ground state is observable in solution ($g_\perp > g_\parallel$, EPR).

Unlike the tris(xanthate), $Ni(txn)_3^-$ is unstable in solution, affording the new stable trithiocarbonate-chelated and thiolate-bridged dimer $Ni_2(SEt)_2(CS_3)_2^{2-}$, which has been isolated and structurally characterized as the Et_4N^+ salt. A rationale for the unusual chemical transformation is proposed. The dimer incorporates a pair of edge-sharing NiS_4 planes. Among species having this structural feature, the Ni···Ni length is found to be correlated in a relatively simple manner to the dihedral angle between the NiS_4 planes.

Experimental Section

Materials. Potassium ethyl thioxanthate was synthesized according to a reported procedure.[6a] The solvent and the supporting electrolyte for electrochemical work were prepared/purified as before.[24] All other chemicals and solvents are used as received.

Physical Measurements. Microanalytical data (C, H, N) were obtained with a Perkin-Elmer Model 240C elemental analyzer. Electronic spectra were recorded with a Hitachi 330 spectrophotometer. EPR spectra were recorded in the X-band with a Varian E-109C spectrometer, and electrochemical measurements were done using the PAR Model 370-4 electrochemistry system as reported earlier.[1]

Table II. Crystallographic Data for $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$

chem formula	$C_{22}H_{50}N_2S_8Ni_2$	Z	8
fw	716.5	T, K	296
space group	$C2/c$	λ, Å	0.71073
a, Å	31.279 (9)	ρ_{calcd}, g cm^{-3}	1.350
b, Å	13.670 (5)	μ, cm^{-1}	15.44
c, Å	16.900 (4)	min transm coeff[c]	0.8399
β, deg	102.63 (2)	R[a]	0.0733
V, Å^3	7050 (4)	R_w[b]	0.0720

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2|F_o|$. [c] Maximum normalized to 1.0.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^3) for the Anion of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$

atom	x	y	z	U(eq)
Ni(1)	1172 (1)	496 (2)	5115 (1)	113 (1)
Ni(2)	783 (1)	2113 (2)	5641 (1)	106 (1)
S(1)	2380 (3)	−1044 (9)	5137 (6)	326 (7)
S(2)	1678 (2)	375 (5)	4421 (3)	165 (3)
S(3)	1613 (2)	−560 (4)	5827 (3)	157 (3)
S(4)	1071 (2)	4811 (4)	7047 (3)	172 (3)
S(5)	920 (2)	3653 (3)	5493 (3)	141 (3)
S(6)	840 (2)	2673 (3)	6864 (2)	120 (2)
S(7)	737 (2)	1574 (3)	4400 (3)	122 (2)
S(8)	667 (2)	562 (3)	5828 (3)	128 (2)
C(1)	1933 (7)	−488 (18)	5173 (14)	177 (7)
C(2)	960 (6)	3803 (13)	6497 (10)	128 (8)
C(3)	1036 (8)	2347 (15)	3855 (11)	177 (13)
C(4)	744 (7)	3083 (17)	3321 (13)	261 (21)
C(5)	862 (8)	215 (18)	6863 (11)	194 (15)
C(6)	548 (10)	−419 (20)	7240 (14)	284 (23)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Synthesis of Complexes. a. Tetraethylammonium Tris(ethyl thioxanthato)nickelate(II) $[Et_4N][Ni(txn)_3]$. To an aqueous solution (20 mL) of potassium ethyl thioxanthate (1.126 g, 6.4 mmol) and an excess of tetraethylammonium chloride (1.5 g) was added an aqueous solution (20 mL) of hexaaquo nickel(II) chloride (475 mg, 2.0 mmol) dropwise. The desired complex precipitated with the addition of every drop. Finally the solid was filtered off and was washed with cold water and then dried over P_4O_{10} under vacuo. Anal. Calcd for $C_{17}H_{35}NS_9Ni$: C, 34.02; H, 5.84; N, 2.33. Found: C, 34.11; H, 5.71; N, 2.41. Yield, 90%.

b. Tetraethylammonium Bis(Trithiocarbonato)bis(μ-ethylthio)dinickelate(II), $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$. To an aqueous (20 mL) suspension of $[Et_4N][Ni(txn)_3]$ (600 mg, 1.0 mmol) was added acetone (20 mL), and the mixture was stirred vigorously for 30 min. It was then filtered, and the clear greenish brown filtrate was allowed to evaporate to produce the crystalline compound. Anal. Calcd for $C_{22}H_{50}N_2S_8Ni_2$: C, 36.90; H, 6.99; N, 3.91. Found: C, 36.78; H, 6.68; N, 3.75. Yield, 70%.

The residue from filtration was a brown amorphous mass insoluble in organic solvents and water. The chemical nature of this material is not clear at present. Anal. Found: C, 48.38; H, 8.47; S, 34.19; Ni, 9.82.

X-ray Structure Determination. The cell parameters of a crystal of $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ (0.60 × 0.42 × 0.40 mm^3), grown by slow diffusion of acetone solution into hexane, was determined by a least-squares fit of 25 machine-centered reflections (2θ, 15–25°). The lattice dimension and Laue group were checked by axial photography. Data were collected by the ω-scan method (2θ, 2–45°) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction during the ~50 h exposure to X-rays. Data were corrected for Lorentz–polarization effects, and an empirical absorption correction was done on the basis of azimuthal scans of six reflections.[25] Systematic absences suggested the space group Cc or $C2/c$; refinement was successfully completed in $C2/c$. Of the 3755 unique reflections, 1964 satisfying $I > 3\sigma(I)$ were used for structure solution by direct methods. All the non-hydrogen atoms of the anion

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were made anisotropic. The thermal parameters were quite large. The tetraethylammonium cations were disordered, and here the non-hydrogen atoms were treated isotropically. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. All refinements were performed by full-matrix least-squares procedures. The highest residual was 0.34 e Å^{-3}. Calculations were done on a MicroVAX II computer with the programs of SHELXTL-PLUS.[26] Significant crystal data are listed in Table II. Atomic coordinates are collected in Table III.

Acknowledgment. Crystallography was performed in the National Single Crystal Diffractometer Facility established at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, by the Department of Science and Technology, New Delhi. Financial support received from the Council of Scientific and Industrial Research is also acknowledged.

Supplementary Material Available: Complete atomic coordinates (Table SI), bond distances (Table SII) and angles (Table SIII), anisotropic thermal parameters (Table SIV), and hydrogen atom positional parameters (Table SV) for $[\mathrm{Et_4N}]_2[\mathrm{Ni_2(SEt)_2(CS_3)_2}]$ (3 pages); a listing of observed and calculated structure factors for the above complex (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Synthetic Chemistry, Faculty of Engineering,
University of Tokyo, Bunkyo-ku, Hongo, Tokyo 113, Japan

Spontaneous Fixation of Carbon Dioxide in Air by a Nickel Diamine Complex: Synthesis and Characterization of a Trinuclear Nickel(II) Complex with a Novel Hydrogen Bonding System around a Carbonate Ligand

Tomoaki Tanase,*[1a] Sadao Nitta, Sadao Yoshikawa,[1b] Kimiko Kobayashi,[1c] Tosio Sakurai,[1d] and Shigenobu Yano*[1e]

Received February 21, 1991

The nickel(II) complex of *N,N*-dimethylethylenediamine (*N,N*-Me$_2$en), $[\mathrm{Ni}(N,N\text{-}\mathrm{Me_2en})_3](\mathrm{ClO_4})_2$ (**1**), in aqueous ethanol spontaneously adsorbed and fixed CO$_2$ in air to give a trinuclear nickel(II) complex, $[\mathrm{Ni_3}(N,N\text{-}\mathrm{Me_2en})_6(\mathrm{CO_3})(\mathrm{H_2O})_4](\mathrm{ClO_4})_4$ (**2**). The complex **2** crystallizes in the hexagonal system, space group $P6_3$, with $a = 25.824$ (7) Å, $c = 14.506$ (3) Å, and $Z = 6$. The structure was solved by direct methods and refined by least-squares techniques to a final R value of 0.065 for 2940 independent reflections with $F_o > 3\sigma(F_o)$. The absolute configuration was determined by the Bijvoet method. The complex cation is trinuclear, which is made up of three octahedral nickel(II) complexes, Λ-*cis*-(*O,O*)-$[\mathrm{Ni}(N,N\text{-}\mathrm{Me_2en})_2(\mathrm{CO_3})]$ and Λ- and Δ-*cis*-(*O,O*)-$[\mathrm{Ni}(N,N\text{-}\mathrm{Me_2en})(\mathrm{H_2O})_2]^{2+}$, joined by a novel hydrogen bonding network around the coordinating carbonate ligand. This planar hydrogen bonding system might stabilize the bidentate carbonate, resulting in the spontaneous fixation of CO$_2$ in air. When analogous diamines (*N,N'*-dimethylethylenediamine, *N,N*-diethylethylenediamine, *N*-methylethylenediamine, *N*-ethylethylenediamine) were used instead of *N,N*-Me$_2$en, no fixation of CO$_2$ was observed. The N-substituent of diamines is an important factors in determining the occurrence of CO$_2$ uptake.

Introduction

The chemistry of CO$_2$ has been the subject of considerable investigative attention for a variety of reasons including its potential as a C1 feedstock,[2] the increase in atmospheric CO$_2$ concentration,[3] and its possible use as a substrate for storing solar energy.[4] In this regard, the fixation of CO$_2$ under mild conditions by transition metal complexes and its conversion into useful chemical compounds are significant subjects in inorganic chemistry. A number of transition metal complexes containing CO$_2$[5–9] and their derivatives (carbonate,[10–12] alkyl carbonate,[13–15] carbamate[15,16]) have been prepared and characterized. However, most of these complexes were air-sensitive and not suitable for CO$_2$ fixation under atmospheric conditions. Thus far studies concerning spontaneous

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(1) Present address: (a) Department of Chemistry, Faculty of Science, Toho University, Funabashi-shi, Chiba 274, Japan. (b) Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, Japan. (c) Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan. (d) Faculty of Education, Shinshu University, Hishinagano, Nagano 593, Japan. (e) Department of Chemistry, Faculty of Science, Nara Women's University, Nara-shi, Nara 630, Japan.

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