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Notes

Variable Valence MnO_3S_3 Species. The Case of Tris(1-hydroxy-2-pyridinethionato)manganese(II,III,IV) and Its Structural Correlation with the Cobalt(III) Analog

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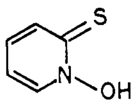
This work stems from our interest in variable oxidation states of manganese.[1-3] Our study[4] on tris(thiohydroxamates)[5] as the first MnO_3S_3 species spanning the metal oxidation states +2 to +4 has received attention particularly in relation to EPR spectra of manganese(IV) species.[6] No other variable valence MnO_3S_3 system has, however, been reported so far. This has prompted us to briefly present another example of the MnO_3S_3 system in the form of the redox triad MnL_3^z ($z = 0, \pm1$) incorporating the fungitoxic O,S ligand 1-hydroxy-2-pyridinethione, HL (**1**).[7-13]



HL

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Metal redox and EPR spectra of the system are examined and compared with those of tris(thiohydroxamates).[4] The facial nature of MnL_3 is established via isomorphism with CoL_3 which has been structurally characterized.

Results and Discussion

Synthesis and Geometry of MnL_3. This complex was synthesized in excellent yield by the reaction of NaL with $Mn(CH_3CO_2)_3{\cdot}2H_2O$ in methanol. Reaction with $Mn(CH_3CO_2)_2{\cdot}4H_2O$ followed by aeration affords the same product. Selected characterization data are given in Table I. The only reported manganese complex of HL is MnL_2.[8]

Single crystals of MnL_3 could not be grown. However, $CoL_3{\cdot}CHCl_3$ afforded good crystals, and it has been structurally characterized. A view of the chelate molecule and selected bond parameters are shown in Figure 1. The CoO_3S_3 coordination sphere has facial geometry, the trigonal twist angle between the O_3 and S_3 faces being 54.6°. The average C–S length of 1.720 (5) Å is in agreement with the thione form,[12] as in **1**.

It has also been possible to grow single crystals of the mixed metal system $Co_{(1-x)}Mn_xL_3{\cdot}CHCl_3$ with upto about 20 atom % of manganese ($x = 0.2$) by cocrystallization. The unit cell of a crystal with $x = 0.2$ is found to be isometric with that of $CoL_3{\cdot}CHCl_3$ (Table II). We conclude that MnL_3 also has facial geometry.[14,15] Significantly the IR spectra of MnL_3 and CoL_3 have a 1:1 correspondence with each other except for shifts of bands (300–3500 cm^{-1}). Facial geometry of MO_3S_3 (M = Mn, Co) sphere is a feature common to both ML_3 and tris(thiohydroxamates).[5]

The MnL_3^z ($z = 0, \pm1$) Redox Series. Voltammetry of MnL_3 was performed at platinum working electrode in 2:1 mixture of acetonitrile and dichloromethane[16] revealing two one-electron couples, eqs 1 and 2. The near reversibility (peak-to-peak separation, ΔE_p, 60–70 mV) of the couples of eqs 1 and 2 suggests that the redox processes are stereoretentive and all the three MnL_3^z species have the same gross geometry for the MnO_3S_3 coordination spheres (facial).

$$Mn^{IV}L_3^+ + e \rightleftharpoons Mn^{III}L_3 \qquad (1)$$

$$Mn^{III}L_3 + e \rightleftharpoons Mn^{II}L_3^- \qquad (2)$$

The species MnL_3^+ and MnL_3^- can be quantitatively generated in solution by exhaustive electrolysis of MnL_3 at +0.70 and −0.35 V vs SCE, respectively. With appropriately set initial potential and scan direction the voltammograms of both these species are virtually identical to that of MnL_3 as shown in Figure 2. Although electrogenerated solutions of MnL_3^+ and MnL_3^- are stable for at least 1 h under nitrogen, we have not succeeded in isolating them as pure salts. The magnetic properties of the pair have been studied using electrogenerated solutions, vide infra. Characteristic electronic spectral features of MnL_3^+ are listed in Table I.

The $E_{1/2}$ values of the couples of eqs 1 and 2 are respectively +0.37 and −0.07 V vs SCE. In tris(thiohydroxamates) of manganese the corresponding reduction potentials are significantly lower.[4] This suggests[3] that L^- is a weaker donor than thiohydroxamate anions.

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(1) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423.

(2) Chandra, S. K.; Choudhury, S. B.; Ray, D.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1990**, 474.

(3) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4031 and references cited therein.

(4) Pal, S.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 3037.

(5) Freyberg, D. P.; Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 3037.

(6) (a) Saadeh, S. M.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8. Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Ibid.* **1987**, *26*, 2487. Kessissoglou, D. P.; Butler, W. M.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1253. (b) Chan, M. K.; Armstrong, W. H. *Inorg. Chem.* **1989**, *28*, 3779. (c) Koikawa, M.; Okawa, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1988**, 641.

(7) Sijpestejn, A. K.; Janssen, M. J. *Nature* **1958**, *182*, 1313.

(8) Robinson, M. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1277 and references cited therein.

(9) West, D. X.; Frank, C. A. *J. Inorg. Nucl. Chem.* **1979**, *41*, 49. Brown, D. A.; West, D. X. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1017. Liu, W. S.; Bunting, R. K.; West, D. X. *Inorg. Chim. Acta* **1985**, *105*, 177. West, D. X.; Hines, J. L.; Bunting, R. K.; Symmons, M. C. R.; Malik, N. A. *Inorg. Chim. Acta* **1988**, *143*, 229.

(10) Davison, J. L.; Preston, P. L.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1983**, 783.

(11) Barnett, B. L.; Kretschmar, H. C.; Hartman, F. A. *Inorg. Chem.* **1977**, *16*, 1834.

(12) Casellato, U.; Vigato, P. A.; Tamburini, S.; Graziani, R.; Vidali, M. *Inorg. Chim. Acta* **1983**, *72*, 141. Casellato, U.; Sitran, S.; Tamburini, S.; Vigato, P. A.; Graziani, R. *Inorg. Chim. Acta* **1984**, *95*, 37.

(13) Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1991**, *30*, 519.

(14) Sizable deviation from idealized C_3 geometry may be anticipated due to d^4 Jahn–Teller distortion.[15] The low-energy ligand field band of MnL_3 (Table I) is indicative of the Jahn–Teller splitting of the e orbital. Distortion may be one of the reasons for the different crystallization behavior of pure CoL_3 and MnL_3. The cobalt complex crystallizes well as the chloroform adduct and can also accommodate MnL_3 upto a certain level of substitution. But MnL_3 alone fails to afford good crystals.

(15) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 704. (b) Davis, T. S.; Fackler, J. P.; Weeks, M. J. *Inorg. Chem.* **1968**, *7*, 1994.

(16) Electrochemical studies on MnL_3 were also made in pure dichloromethane, and the same two voltammetric features are observed but the reversibility is poorer ($\Delta E_p \sim$ 160 mV). Pure acetonitrile could not be used as a solvent due to lack of solubility of MnL_3 in it.

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Table I. Characterization Data

compd	electronic spectral data[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	μ_{eff}, μ_B (in soln[a])	g values[b]
MnL_3	1400 (160), 700 (650)	5.00[c]	*d*
MnL_3^+	560 (3400), 480 (2400), 410 (2800)	4.01	4.381, 2.004
MnL_3^-	*e*	6.10	5.055, 2.987,[f] 1.611

[a] In dichloromethane at 300 K. [b] In dichloromethane–toluene (1:1) glass (77 K). [c] The magnetic moment of solid MnL_3 is 4.99 μ_B. [d] EPR-silent. [e] No significant bands observed in the range 450–1500 nm. [f] This signal has six hyperfine lines with an average *A* value of 88 G.

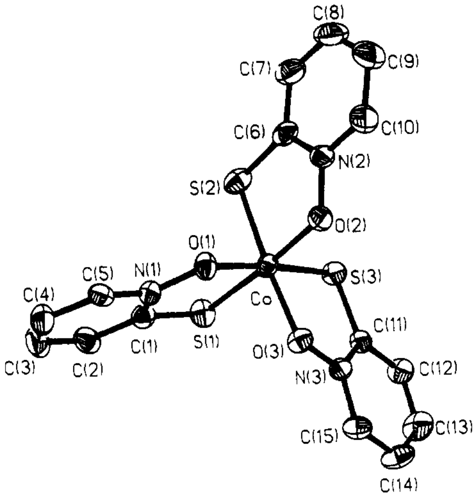

Figure 1. Perspective view and atom-labeling scheme of CoL_3. Atoms are shown as their 30% probability ellipsoid. Selected distances (Å) and angles (deg): Co–S(1), 2.205 (2); Co–S(2), 2.193 (2); Co–S(3), 2.205 (2); Co–O(1), 1.932 (3); Co–O(2), 1.940 (3); Co–O(3), 1.923 (3); S(1)–Co–O(1), 88.1 (1); S(3)–Co–O(2), 94.8 (1); S(1)–Co–S(3), 92.1 (1); O(1)–Co–O(2), 85.1 (1); S(2)–Co–O(1), 94.5 (1); S(2)–Co–O(3), 175.6 (1).

Table II. Unit Cell Parameters

	$CoL_3 \cdot CHCl_3$[a]	$Co_{0.8}Mn_{0.2}L_3 \cdot CHCl_3$[b]
cryst syst	monoclinic, *P*	monoclinic, *P*
a, Å	9.384 (3)	9.382 (4)
b, Å	15.207 (7)	15.205 (9)
c, Å	15.441 (6)	15.471 (7)
β, deg	96.09 (3)	95.90 (4)
V, Å^3	2192 (2)	2195 (2)

[a] The size of the crystal was 0.42 × 0.42 × 0.47 mm^3. [b] Crystal size 0.35 × 0.34 × 0.38 mm^3.

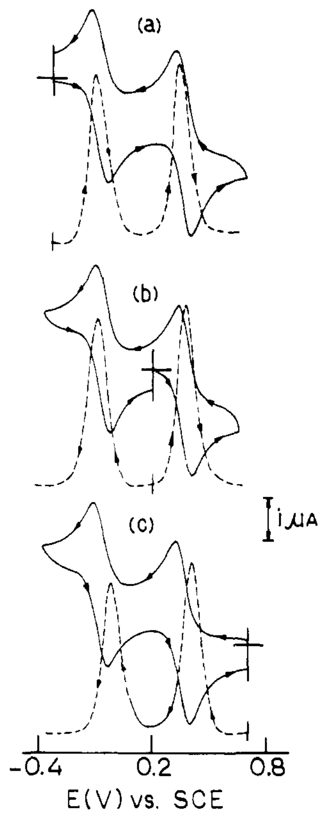

Figure 2. Cyclic (—) (scan rate 50 mVs^{-1}) and differential pulse (- - -) (scan rate 10 mVs^{-1}, modulation amplitude 25 mV) voltammograms of a ~10^{-3} M solutions (a) $Mn^{II}L_3^-$, (b) $Mn^{III}L_3$ and (c) $Mn^{IV}L_3^+$ in a dichloromethane–acetonitrile (1:2) mixture (0.1 M TEAP) at a platinum electrode (298 K). Marked current range is 5 μA for cyclic and 2 μA for differential pulse voltammetry.

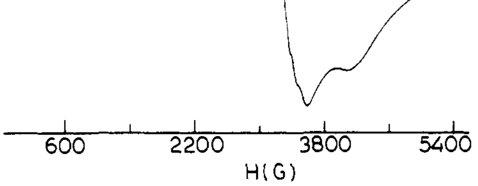

Figure 3. X-Band EPR spectra for (a) $Mn^{IV}L_3^+$ and (b) $Mn^{II}L_3^-$ in dichloromethane–toluene (1:1) glass (77 K).

Magnetism and EPR Spectra. Solution magnetic moments of MnL_3^z determined by the Evans method[17] are listed in Table I. The values correspond to $S = {}^3/_2$, 2 and ${}^5/_2$ for $z = +1$, 0, and -1, respectively. The frozen solution (77 K) EPR spectra of MnL_3^+ and MnL_3^- are shown in Figure 3; MnL_3 is EPR-silent as expected for the high-spin d^4 configuration.[1,3]

The facial MnO_3S_3 coordination sphere can be considered as an axially (idealized C_3) distorted octahedron. In crystal field of O_h symmetry, manganese(IV) (d^3) has a $^4A_{2g}$ ground state which affords an isotropic resonance at $g \sim 2$.[18] In axially distorted complexes with the zero-field splitting parameter *D* large compared to the microwave quantum (0.31 cm^{-1} for X-band) two main resonances are expected: a strong one near $g = 4$ and a weaker one near $g = 2$.[19] The spectrum of MnL_3^+ belongs to this category. In contrast, tris(thiohydroxamates) of manganese(IV) belong to the case $2D \ll h\nu$ (strong signal near $g = 2$ and weaker signal near $g = 4$).[4]

The spectrum of the MnL_3^- ion is also in general agreement with strong axial distortion for the $S = {}^5/_2$ ion.[20,21] Here ^{55}Mn hyperfine structure is partially resolved in the signal near $g = 2$.

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

(18) (a) Moews, P. *Inorg. Chem.* **1966**, *5*, 5. (b) McGarvey, B. R. In *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 3; p 89. (c) Richeas, D. T.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3681.

(19) (a) Pederson, E.; Toftlund, H. *Inorg. Chem.* **1974**, *13*, 1603. (b) Bradley, D. C.; Copperthwaite, R. G.; Cotton, S. A.; Sales, K. D.; Gibson, E. J. F. *J. Chem. Soc., Dalton Trans.* **1973**, 191. (c) Hampel, J. C.; Morgan, L. O.; Lewis, L. B. *Inorg. Chem.* **1970**, *9*, 2064.

(20) Basu, P.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1988**, *27*, 1850.

(21) (a) Wickman, H. H.; Klein, M. P.; Shirley, D. A. *J. Chem. Phys.* **1965**, *42*, 2113. (b) Dowsing, R. D.; Gibson, J. F. *J. Chem. Phys.* **1969**, *50*, 294. (c) Dowsing, R. D.; Gibson, J. F.; Goodgame, M.; Hayward, P. J. *J. Chem. Soc. A* **1969**, 187.

Conclusions. The MnL_3^z ($z = 0, \pm 1$) system representing a new example of the rare variable valence MnO_3S_3 family has been synthesized and characterized by isolation and/or redox and spectral studies in solution. Facial geometry is revealed by structure determination of $CoL_3{\cdot}CHCl_3$ and the result is extended to MnL_3 via isomorphous substitution and electrochemical reversibility. Compared to tris(thiohydroxamates), the MnL_3^z system has higher metal reduction potentials and stronger axial distortions.

Experimental Section

Materials. The sodium salt of the ligand 1-hydroxy-2-pyridinethione was used as received from Fluka AG, Switzerland. The purification of dichloromethane and acetonitrile and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as before.[22] $Mn(CH_3CO_2)_3{\cdot}2H_2O$ was prepared as reported.[23] All other chemicals and reagents used for preparative work were of reagent grade.

Physical Measurements. Electronic spectra were recorded using a Hitachi 330 spectrophotometer. Infrared spectra were taken on a Perkin-Elmer 783 spectrophotometer. Magnetic susceptibility was measured on a PAR 155 vibrating sample magnetometer. Solution magnetic moments were determined[17] in dichloromethane solution utilizing the shift of the ^1H signal of CH_2Cl_2 in a Bruker 270-MHz spectrometer. X-Band EPR spectra were collected on a Varian E-109C spectrometer fitted with a quartz Dewar flask for low-temperature measurements (liquid nitrogen, 77 K). DPPH ($g = 2.0037$) was used to calibrate the EPR spectra. Electrochemical measurements were done by using a PAR Model 370-4 electrochemistry system as described elsewhere.[22] Microanalytical data (C,H,N) were obtained with a Perkin-Elmer Model 240C elemental analyzer.

Preparation of Complexes. Tris(1-hydroxy-2-pyridinethionato)manganese(III), MnL_3. To a methanolic solution (50 mL) of the sodium salt of ligand, NaL, (1.5 g, 0.01 mol), 0.89 g (0.0033 mol) $Mn(CH_3CO_2)_3{\cdot}2H_2O$ was added with stirring. Immediately a green solid precipitated. The stirring was continued for 15 min. The solid was filtered, washed with methanol and a little water, and dried in vacuo over P_4O_{10}; yield 1.33 g (93%). Anal. Calcd for $C_{15}H_{12}N_3O_3S_3Mn$: C, 41.58; H, 2.77; N, 9.70. Found: C, 41.39; H, 2.63; N, 9.20. IR: ν(NO), 1085; ν(CS), 1145 cm^{-1}.

Alternatively, to a methanolic solution (50 mL) of NaL (1.5 g, 0.01 mol) was added 0.80 g (0.0033 mol) of $Mn(CH_3CO_2)_2{\cdot}4H_2O$. Air was bubbled through this solution for 2 h. The initially colorless solution slowly turned deep green, and a green precipitate deposited. This was filtered and purified as above; yield 1.0 g (70%).

Chloroform Adduct of Tris(1-hydroxy-2-pyridinethionato)cobalt(III), $CoL_3{\cdot}CHCl_3$. To a solution of NaL (1.5 g, 0.01 mol) in methanol (50 mL) was added 0.83 g (0.0033 mol) of $Co(CH_3CO_2)_2{\cdot}4H_2O$. Air was passed through this solution (the color of the solution changed to green) until complete evaporation had occurred. The solid was extracted with chloroform and layered with hexane to yield dark green crystals of $CoL_3{\cdot}CHCl_3$. Yield: 1.47 g (80%). Anal. Calcd for $C_{16}H_{13}N_3O_3S_3Cl_3Co$: C, 34.51; H, 2.35; N, 7.55. Found: C, 34.20; H, 2.32; N, 7.49. IR: ν(NO), 1090; ν(CS), 1150 cm^{-1}. The complex $CoL_3{\cdot}2H_2O$ has been described.[8]

Mixed-Metal Complex: $Co_{0.8}Mn_{0.2}L_3{\cdot}CHCl_3$. A 0.45-g (0.8-mmol) sample of $CoL_3{\cdot}CHCl_3$ and 0.15 g of MnL_3 (0.35 mmol) were dissolved in chloroform (100 mL) and layered with hexane (300 mL). After 2 days single crystals had deposited. Anal. Calcd for $C_{16}H_{13}N_3O_3S_3Cl_3Co_{0.8}Mn_{0.2}$: C, 34.56; H, 2.36; N, 7.56. Found: C, 34.49; H, 2.21; N, 7.42. The percentage of manganese in the crystals was estimated from electronic spectra by monitoring the intensity of the band of MnL_3 at 1400 nm.

Table III. Crystallographic Data for $CoL_3{\cdot}CHCl_3$[a]

chem formula: $C_{16}H_{13}N_3O_3S_3Cl_3Co$	$\rho_{calcd} = 1.69$ g cm^{-3}
fw = 556.78	$\mu = 14.48$ cm^{-1}
space group: $P2_1/n$	transm coeff[b] = 0.9253
$Z = 4$	R[c] = 0.0437
$T = 22 \pm 1$ °C	R_w[d] = 0.0425
$\lambda = 0.710\,73$ Å	

[a] Unit cell parameters a, b, c, β, and V are listed in Table II. [b] Maximum normalized to 1. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(|F_o| + 0.0003|F_o|^2)$.

Electrosynthesis of the Tris(1-hydroxy-2-pyridinethionato)manganese(IV) Cation, MnL_3^+, and the Tris(1-hydroxy-2-pyridinethionato)manganese(II) Anion, MnL_3^-, in Solution. MnL_3 (22.02 mg, 0.05 mmol) in 20 mL of dichloromethane (0.1 M TEAP) was exhaustively oxidized at +0.70 V vs SCE in nitrogen atmosphere affording violet-colored MnL_3^+ (coulomb count: found, 4.68; calcd, 4.91). To generate the virtually colorless MnL_3^- ion, MnL_3 (25.98 mg, 0.06 mmol) taken in 20 mL of dichloromethane (0.1 M TEAP) was reduced at −0.35 V vs SCE in nitrogen atmosphere (coulomb count: found, 5.79; calcd, 5.61).

The MnL_3^+ and MnL_3^- solutions so produced were used for spectral and magnetic measurements. For voltammetric measurements the species were similarly generated using a 1:2 dichloromethane–acetonitrile mixture as the solvent.

X-ray Studies. X-Ray studies were performed on a Nicolet R3m/V automated diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation.

(a) Unit Cell Determination. The unit cell parameters of $CoL_3{\cdot}CHCl_3$ were determined by a least-squares fit of 26 accurately measured reflections ($14° < 2\theta < 28°$). For $Co_{0.8}Mn_{0.2}L_3{\cdot}CHCl_3$, the cell was determined by least-squares fit of 25 automatically centered reflections with $15° < 2\theta < 29°$. The cell parameters are listed in Table II and other crystal data for $CoL_3{\cdot}CHCl_3$ are given in Table III.

(b) Structure of $CoL_3{\cdot}CHCl_3$. Data were collected in the 2θ range 2–52° by the ω-scan method. Two standard reflections were periodically monitored during 40 h of data collection, showing no significant variations of intensity. Data were corrected for Lorentz-polarization effects, and an empirical absorption correction was applied. The minimum transmission was 0.93 (maximum normalized to 1). Systematic absences uniquely afforded the space group $P2_1/n$. 2995 observed ($I > 3\sigma(I)$) data were used for structure solution by the heavy atom method. All non-hydrogen atoms were included in calculated positions ($U = 0.08$ Å^2). The highest difference Fourier peak was +0.26 e Å^{-3}. Computations were carried out on a MicroVAX II computer using SHELXTL-PLUS program system.[24] Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for the seven atoms within the coordination sphere are stated here in the order x, y, z, U(eq): Co, 1646 (1), 2254 (1), 730 (1), 41 (1); S(1), −33 (1), 2367 (1), 1620 (1), 58 (1); S(2), 1246 (2), 841 (1), 556 (1), 62 (1); S(3), 3318 (1), 2008 (1), 1818 (1), 51 (1); O(1), 231 (3), 2599 (2), −209 (2), 48 (1); O(2), 2941 (3), 2171 (2), −166 (2), 49 (1); O(3), 2125 (3), 3485 (2), 834 (2), 48 (1).

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Supplementary Material Available: Tables SI–SVI listing crystallographic data, positional parameters, anisotropic thermal parameters, complete bond distances, complete bond angles, and H-atom positional parameters (9 pages). Ordering information is given on any current masthead page.

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[22] Pramanik, A.; Bag, N.; Ray, D.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 410.

[23] Brauer, G., Ed. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965; Vol. 2, p 1469.

[24] Sheldrick, G. M. SHELXTL-PLUS 88, Structure Determination Software Programs. Nicolet Instrument Corp.; Madison, WI, 1988.