Inorganica Chimica Acta, *119* (1986) 121 –126

Crystal and Molecular Structure of Racemic *fac*-Tris-(*S*-methylisopropylidenehydrazinecarbodithioato)cobalt(III), $Co(NS)_3$, and the Kinetics of its Isomerization in Aprotic Solvents

KAY D. ONAN*, GEOFFREY DAVIES

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

MOHAMED A. EL-SAYED and AHMED EL-TOUKHY*

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

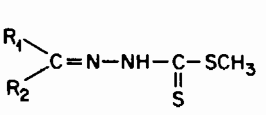
(Received February 14, 1986; revised April 28, 1986)

Abstract

The crystal and molecular structure of *fac*-tris-(*S*-methylisopropylidenehydrazinecarbodithioato)cobalt(III) is reported. The dark olive-green $Co(NS)_3$ crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ in a cell of dimensions $a = 17.876(2)$, $b = 9.792(2)$, $c = 14.816(2)$ Å and $\beta = 108.63(1)°$. The coordination sphere is relatively undistorted but the cobalt atom does not lie in the center of this sphere. Kinetic studies have shown the *fac* to *mer* isomerization to have a very large (⩾100) equilibrium constant and to proceed by a trigonal twist mechanism.

Introduction

Variation of R_1 and R_2 in *S*-methylhydrazinecarbodithioate Schiff bases, HNS, strongly influences the manner in which they react with metal salts and the properties of the complexes formed [1–5].

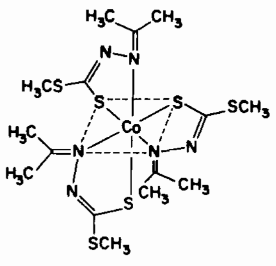


HNS

– Nickel salts react with an aldehydic ligand (R_1 = Ph, R_2 = H) to form a *trans*-square planar [6] complex, while the product with $R_1 = R_2 = CH_3$ is a *cis*-complex with a flattened tetrahedral geometry [7].
– The stoichiometries of adducts $Ni(NS)_2 \cdot B_n$ formed with monodentate Lewis bases B are different ($n = 2$ for aldehydic, $n = 1$ for ketonic ligands) [2].
– Aldehydic ligands react with $CuCl_2$ in alcohols at room temperature to give $Cu^{II}(NS)_2$ products, while ketonic ligands give $Cu^I(HNS)_2Cl$ [3].
– The *S*-methyl groups of $M(NS)_2$ complexes are replaceable with primary or secondary amines only when NS^- is an aldehydic ligand [5].
– The products of and rate laws for transmetalation [8] of polynuclear copper complexes by $M(NS)_2$ reagents depend on the ligand type [9, 10].

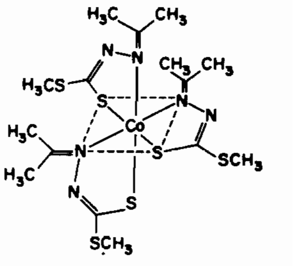
Aldehydic ligands allow easy formation of brown cobalt(III) complexes, $Co(NS)_3$, whose spectra are the same whether in the solid state or in solution. Proton NMR measurements indicate that they are *mer*-isomers [1]. By contrast, ketonic ligands only permit the formation of $Co(NS)_2$, except when $R_1 = R_2 = CH_3$; $Co(NS)_3$ can form in this case because of the smaller R groups [1]. However, the isolated product is olive green instead of brown, though it does turn brown within a few minutes of dissolution.

We have found that $Co(NS)_3$ complexes with aldehydic ligands are not transmetalating agents for polynuclear copper complexes whereas I and/or II are. Since we are interested in the relationship between *fac*- and *mer*-isomers of this type and the influence of structure on mechanisms of transmetalation reactions [9], we report the crystal and molecular structure of racemic *fac*-tris(*S*-methylisopropylidenehydrazinecarbodithioato)cobalt(III), I, and the kinetics of its isomerization to the *mer*-isomer, II, in methylene chloride and nitrobenzene.



fac

I



mer

II

---

*Authors to whom correspondence should be addressed.

0020-1693/86/$3.50

Experimental

Materials

The purification of methylene chloride, nitrobenzene (Aldrich), methanol (Baker) and diethylether (Fisher) followed literature procedures [8]. *S*-Methylisopropylidenehydrazinecarbodithioate, HNS, was prepared as previously described [11]. The title complex was prepared by adding a clear solution of cobalt(II) acetate tetrahydrate (0.01 mol) in methanol (30 ml) to a solution of HNS (0.03 mol) in methanol (30 ml). The reaction mixture was flushed with dioxygen and refluxed for 30 min. The olive green cobalt(III) complex (**I**) which precipitated on cooling was filtered and washed with methanol and diethylether. Crystallization from methylene chloride/diethylether gave dark olive-green single crystals of dimensions suitable for structural characterization.

Crystal Data

$CoC_{15}H_{27}N_6S_6$, $M = 542.7$, monoclinic, $a = 17.876(2)$, $b = 9.792(2)$, $c = 14.816(2)$ Å, $\beta = 108.63(1)°$, $U = 2457.5(6)$ Å^3, $Z = 4$, $D_c = 1.467$ g cm^{-3}, $F(000) = 1128$, Cu Kα radiation ($\lambda = 1.5418$ Å). Space group $P2_1/c$ by systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

Crystallographic Measurements and Structure Solution

Cell dimensions were obtained by a least-squares fit of 15 reflections ($62 < 2\theta < 92°$) measured on a Syntex $P2_1$ automated diffractometer. One quadrant of data with $2\theta \leqslant 130°$ was collected using $\theta/2\theta$ scans and a variable scanning rate. The data were corrected for Lorentz and polarization effects. An empirical absorption correction, determined from a ψ scan, was also made. The ψ scan indicated a maximum drop in intensity of 60%. The reflections with $I \geqslant 2\sigma(I)$ were used in structure solution and refinement.

The structure was solved via Patterson and Fourier syntheses. Full-matrix least-squares were used to refine positional and thermal parameters (anisotropic for non-hydrogen atoms, isotropic for hydrogen atoms)*. Convergence was reached at $R = 0.066$ over 2994 reflections.

The atomic scattering factors for the non-hydrogen atoms were taken from ref. 13 with Co and S being corrected for anomalous scattering [14]. Scattering factors for hydrogen were taken from ref. 15. See also 'Supplementary Material'.

Physical Measurements

Electronic spectral measurements were made with a Beckman DK-1A spectrophotometer in matched quartz cells at room temperature. Isomerization of $(1-10) \times 10^{-3}$ M of the title complex was monitored at 540 nm in methylene chloride or nitrobenzene in the thermostated cell compartment of the Beckman DK-1A spectrophotometer. Pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes of linear plots of $\ln(A_\infty - A_t)$ *vs.* time, where A_t is the absorbance at time t.

Results and Discussion

Crystal and Molecular Structure of (I)

The X-ray diffraction analysis has proved that, in the solid state, tris-(*S*-methylisopropylidenehydrazinecarbodithioato)cobalt(III) occurs as the *fac*-isomer (configuration number 22). This is despite the fact that the equilibrium constant for the isomerization of the *fac*- to the *mer*-isomer is ⩾100 at room temperature (see below). A view of this complex is shown in Fig. 1. The unprimed ligand is labelled A, the singly primed ligand is labelled **B**, and the doubly primed ligand is labelled **C**. Final atomic positional parameters are in Table I, bond lengths and angles are in Table II, and atomic deviations from some mean planes are in Table III.

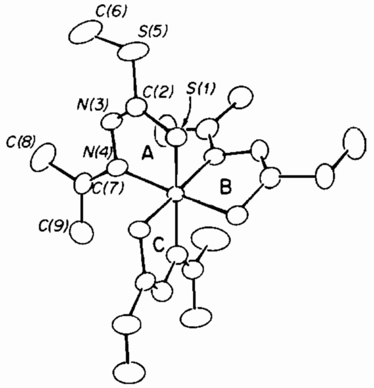


Fig. 1. Molecular structure of *fac*-tris-(*S*-methylisopropylidenehydrazinecarbodithioato)cobalt(III), showing the labelling scheme. Thermal ellipsoids are drawn at the 50% probablity level.

The octahedral coordination sphere is distorted due to the small S—Co—N bite angles of the bidentate ligands (mean 85.6°); also *trans* sulfur and nitrogen atoms assume S—Co—N angles of *ca.* 169° (range 167.9(1)° to 169.6(2)°). The three *cis* sulfur atoms define a plane which is nearly parallel to that of the donor N atoms (1.6° deviation). These planes are rotated very nearly 60° with respect to one another from an eclipsed conformation. The S···S separations are all *ca.* 3.01 Å; the S···N separations, save

---

*All crystallographic calculations were carried out on a VAX 11/780 computer. For the principal programs used see ref. 12.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms in I; Estimated Standard Deviations in Parentheses

Atom	*x/a*	*y/b*	*z/c*
Co	2317.8(5)	1466(1)	730.5(6)
S(1)	3338(1)	1826(2)	2044(1)
C(2)	3867(3)	2807(7)	1493(5)
N(3)	3611(3)	3331(6)	656(4)
N(4)	2795(3)	3079(5)	186(3)
S(5)	4852(1)	3058(3)	2188(2)
C(6)	5189(5)	4244(11)	1481(7)
C(7)	2497(3)	3936(7)	−499(4)
C(8)	2978(5)	5034(9)	−755(5)
C(9)	1649(4)	3876(8)	−1111(5)
S(1′)	1937(1)	−70(2)	1563(1)
C(2′)	2604(3)	−1269(6)	1483(4)
N(3′)	3077(3)	−1223(5)	980(4)
N(4′)	2997(3)	−19(5)	420(3)
S(5′)	2619(1)	−2731(2)	2194(1)
C(6′)	3188(6)	−3919(9)	1772(6)
C(7′)	3461(3)	−56(7)	−94(4)
C(8′)	4026(4)	−1223(8)	−28(6)
C(9′)	3441(4)	982(8)	−829(5)
S(1″)	1699(1)	3023(2)	1347(1)
C(2″)	768(3)	2673(7)	587(5)
N(3″)	584(3)	1861(5)	−127(4)
N(4″)	1237(3)	1206(5)	−294(3)
S(5″)	6(1)	3523(2)	870(2)
C(6″)	−836(4)	3163(10)	−144(8)
C(7″)	988(3)	427(7)	−1040(4)
C(8″)	132(4)	275(9)	−1592(5)
C(9″)	1517(5)	−375(10)	−1400(6)

TABLE II. Interatomic Bond Lengths (A) and Valency Angles (deg) in I; Estimated Standard Deviations are in Parentheses

(a) Bond lengths

	Unprimed	Primed	Double primed
Co–S(1)	2.225(2)	2.172(2)	2.225(2)
Co–N(4)	2.060(5)	2.023(5)	2.052(5)
S(1)–C(2)	1.713(7)	1.692(6)	1.715(6)
C(2)–N(3)	1.280(9)	1.286(8)	1.274(9)
C(2)–S(5)	1.745(7)	1.760(6)	1.746(6)
N(3)–N(4)	1.418(7)	1.413(7)	1.411(7)
N(4)–C(7)	1.288(8)	1.285(8)	1.293(8)
S(5)–C(6)	1.780(10)	1.771(9)	1.786(11)
C(7)–C(8)	1.488(11)	1.497(10)	1.490(9)
C(7)–C(9)	1.494(9)	1.473(10)	1.445(11)

(b) Valency angles
Coordination sphere

S(1)–Co–N(4)	84.1(1)	N(4)–CO–N(4″)	102.2(2)
S(1)–Co–S(1′)	85.9(1)	S(1′)–Co–N(4′)	87.4(1)
S(1)–Co–N(4′)	85.9(1)	S(1′)–Co–S(1″)	87.3(1)
S(1)–Co–S(1″)	84.8(1)	S(1′)–Co–N(4″)	86.9(1)
S(1)–Co–N(4″)	167.9(1)	N(4′)–Co–S(1″)	169.6(2)
N(4)–Co–S(1′)	169.2(2)	N(4′)–Co–N(4″)	103.4(2)
N(4)–Co–N(4′)	96.0(2)	S(1″)–Co–N(4″)	85.2(1)
N(4)–Co–S(1″)	87.7(1)		

Ligands

	Unprimed	Primed	Double primed
Co–S(1)–C(2)	95.3(2)	94.7(2)	95.6(2)
S(1)–C(2)–N(3)	126.7(5)	128.1(5)	127.4(5)
S(1)–C(2)–S(5)	113.5(4)	113.1(3)	114.3(4)
N(3)–C(2)–S(5)	119.8(5)	118.8(5)	118.3(5)
C(2)–N(3)–N(4)	113.6(5)	113.8(5)	114.3(5)
Co–N(4)–C(3)	15.1(4)	114.4(3)	116.5(4)
Co–N(4)–C(7)	132.8(4)	133.9(4)	133.5(4)
N(3)–N(4)–C(7)	112.1(5)	110.9(5)	109.5(5)
C(2)–S(5)–C(6)	101.9(4)	102.7(4)	102.4(4)
N(4)–C(7)–C(8)	122.4(6)	121.7(6)	122.6(6)
N(4)–C(7)–C(9)	122.4(6)	112.9(6)	122.8(6)
C(8–C(7)–C(9)	115.2(6)	115.2(6)	114.6(6)

(c) Intercomplex separations[a] < 3.7 A

N(3)···C(6′)	3.34	N(4)···C(6′)	3.66
C(2)···C(6′)	3.47		

[a] The second atom in each interaction is part of the complex at *x*, 1 + *y*, *z*.

TABLE III Distances (A) of Atoms from Least Squares Planes through Various Groups of Atoms; Atoms Defining the Plane are Italicized

	Ligand A	B	C
Plane 1			
S(1)	0.004	−0.003	−0.001
C(2)	−0.010	0.006	0.003
N(3)	0.010	0.006	−0.003
N(4)	−0.005	0.003	0.001
Co	0.560	−0.311	−0.246

one, are *ca.* 2.90 Å; and the N···N separations, save one, are 3.20 Å. The S(1″)···N(4) separation is relatively long (2.97 Å) and the N(4)···N(4′) separation is relatively short (3.04 Å).

The S–C–N–N atoms of each chelate ring are very nearly planar (Table III) and, in each case, the cobalt lies quite far out of this plane, 0.560 Å from ligand **A** towards N(4′), 0.311 Å from ligand **B** towards S(1) and 0.246 Å out of ligand **C** towards S(1′). Therefore, while the coordination sphere is relatively undistorted, the cobalt atom does not lie in the center of this sphere but is significantly closer to the coordinating atoms in ligand **B**.

The angles between these S–C–N–N planes are not orthogonal but rather take on values of 91.9, 106.4 and 118.7°. However, when the Co atom is included in the definition of each plane, the analogous angles are 74.0°, 98.8° and 89.1°, somewhat closer to orthogonal.

Ligands **A** and **C** exhibit similar Co–S and Co–N bond lengths; in ligand **B**, these lengths, particularly the Co–S distance, are significantly shorter. The Co–S lengths in **A** and **C** are, as expected, slightly shorter than those found in bis-(*S*-methylisopropylidenehydrazinecarbodithiato)cobalt(II), **III** [16], reflecing the difference in radii of Co^{2+} and low spin Co^{3+}. In apparent contradiction to this, the Co–N lengths in **A** and **C** are longer than those in **III**. This lengthening is a result of the structural *trans* effect exerted by the sulfur atom [17]. In $Co(NS)_2$ the interligand S–Co–N angles are far from 180° (mean 125°) [16] while in $Co(NS)_3$ the analogous angles are much closer to 180° (mean 169°).

It is not at all clear why ligand **B** exhibits such short Co–S and Co–N lengths, 2.172(2) and 2.023(5) Å, respectively. These shorter distances are also correlated with a significantly larger bite angle, 87.4(1)° *vs.* 84.1(1) and 85.2(1)°. Because this distortion occurs in just one ligand it does not appear to be due to the lifting of a degeneracy of states. Also, ligand **B** does not appear to suffer close intermolecular contacts which would cause such distortion.

Except for the S(1)–C(2) distances all three ligands are very similar to one another and to those in **III** [16], bis-(*S*-methylisopropylidenehydrazinecarbodithioato)zinc(II), **IV** [16] and, bis-(*S*-methylisopropylidenehydrazinecarbodithioato)nickel(II), **V** [7]. In all these ligands the double bonds are localized. In $Co(NS)_3$, the S(1)–C(2) bonds in ligands **A** and **C** are very similar (1.713(7), 1.715(6) Å) and slightly longer than that in ligand **B** (1.692(6) Å). Though they approximate the calculated length of an S–C(sp^2) bond, they are significantly shorter than those observed in **III, IV** and **V**.

Thus, we have observed that, in the solid state, the *fac*-isomer is the only one present. We propose that the stability gained by the packing of this presumably more polar isomer is sufficient to cause this crystallization.

No other crystal structures have been determined or isomerization reactions observed in other $Co(NS)_3$ systems derived from *S*-methylhydrazinecarbodithioate Schiff bases, all of which seem to exist as *mer*-isomers according to proton NMR data and solid state and solution spectra [1].

Spectrum and Kinetics of Isomerization of I

The solid state spectrum of olive green **I** in silicone grease exhibits a maximum at 620 nm and a shoulder at 590 nm. These same features are observed in aprotic solvents, but on standing at room temperature the green color changes to reddish-brown and the absorbance at 540 nm increases dramatically (Fig. 2). A single isosbestic point is observed at 725 nm, indicating a **I** ⟷ **II** process. Proton NMR measurements have already shown that the product solution contains the *mer*-isomer **II**: three triplets of magnetically inequivalent protons are observed [1].

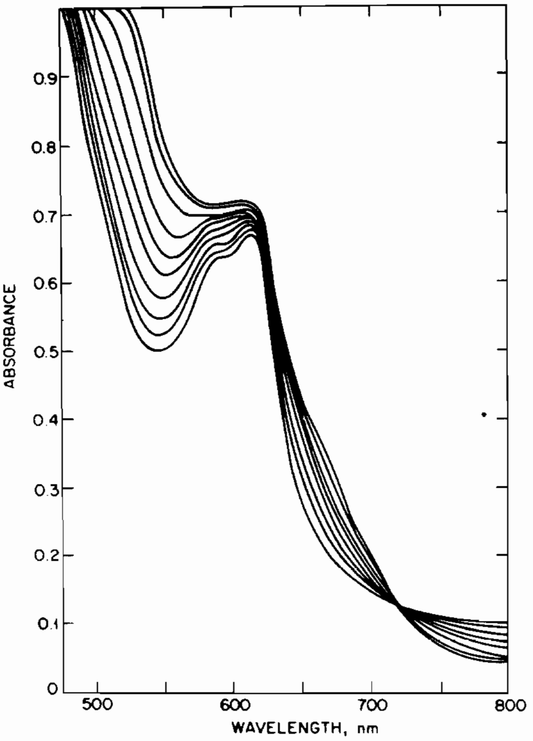


Fig. 2. Spectral changes due to isomerization of **I** (1.0×10^{-3} M) to **II** in nitrobenzene at 10 °C. Spectra were measured each 5 min. An isosbestic is observed at 725 nm.

Plots of $\ln(A_\infty - A_t)$ *vs.* time at 540 nm were linear for at least 4 half-lives (Fig. 3) The total absorbance change on reaction at fixed $[I]_0$ was independent of temperature and proportional to $[I]_0$ at fixed temperature, indicating that K in eqn. (1) is at least 100 at the lowest experimental temperature.

$$I \underset{k_r}{\overset{k_f}{\rightleftharpoons}} II, \quad K \qquad (1)$$

Kinetic data (Table IV) give $\Delta H_f^{\neq} = 16.9 \pm 0.3$, 18.0 ± 0.3 kcal mol^{-1} and $\Delta S_f^{\neq} = -6 \pm 3$, -10 ± 3 cal deg^{-1} mol^{-1} in methylene chloride and nitrobenzene, respectively. There is little kinetic solvent dependence, and the activation parameters are diagnostic of a 'twist' isomerization mechanism [18, 19].

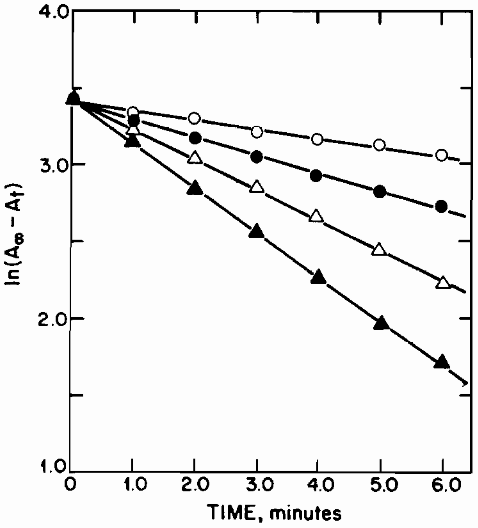


Fig. 3. First-order plots for isomerization of I to II in nitrobenzene at the following temperatures: 12.0, ○; 20.0, ●; 28.0, △; 36.0, ▲.

TABLE IV. Kinetic Data for Isomerization of I in Methylene Chloride and Nitrobenzene

Methylene chloride		Nitrobenzene	
Temperature[a]	$10^2 k_f$[b] ($\min^{-1}$)	Temperature (°C)	$10^2 k_f$[b] ($\min^{-1}$)
3.0	2.3	12.0	3.4
12.0	5.8	20.0	9.3
21.0	15.1	28.0	18.9
29.0	29.3	36.0	30.7

[a]Given in °C, to ±0.1 °C. [b]Maximum standard deviation is ±5% of measured value.

Characteristics of I and II as Transmetalating Agents for Polynuclear Copper Complexes

Like $M(NS)_2$ complexes **III** [10, 16, 20] **IV** [10, 16, 20] and **V** [8–10], cobalt(III) complexes **I** and/or **II** stoichiometrically transmetalate polynuclear copper(I) [21] and copper(II) complexes [22]. Unlike $Co(NS)_3$, the brown $Fe(NS)_3$ complex that we have recently obtained does not appear to isomerize in solution but is also a transmetalating agent [23]. Structural information [6, 7, 16] for such transmetalating agents is necessary for the establishment of transmetalation mechanisms [9, 10, 24].

Transmetalation of copper(I) by cobalt(III) reagents involves redox processes: electron transfer from copper(I) to cobalt(III) precedes transmetalation of $[(DENC)CuX]_4$ complexes (DENC = *N,N*-diethylnicotinamide; X = Cl or Br) by **I** or **II** [21]. Green solutions of **I** and reddish-brown solutions of **II** both rapidly give blue solutions (of cobalt(II)) on mixing with $[(DENC)CuX]_4$ complexes at 0 °C, indicating that electron transfer is faster than isomerization reaction (1).

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom parameters, calculated and observed structure factors and a packing diagram of **I** are available from the authors on request.

Acknowledgements

G.D. thanks the Department of Health and Human Services (Grant RR07143) for financial support. The diffractometer was purchased with assistance from the National Science Foundation. Maher Henary is gratefully acknowledged for experimental assistance.

References

1 L. El-Sayed, A. El-Toukhy and M. F. Iskander, *Transition Met. Chem., 4,* 300 (1979).
2 M. F. Iskander, A. El-Toukhy and M. M. Mishrikey, *J. Inorg. Nucl. Chem., 42,* 361 (1980).
3 M. F. Iskander, L. El-Sayed and A. El-Toukhy, *J. Inorg. Nucl. Chem., 42,* 1145 (1980).
4 M. F. Iskander, L. El-Sayed, L. Labib and A. El-Toukhy, *Inorg. Chim. Acta, 86,* 197 (1984).
5 M. F. Iskander, L. El-Sayed and A. Shehata, to be published.
6 T. Uechi and T. Oniki, *Bull. Chem. Soc. Jpn., 55,* 971 (1982).
7 T. Glowiak and T. Ciszewska, *Inorg. Chim. Acta, 27,* 27 (1978).
8 A. El-Toukhy, G.-Z. Cai, G. Davies, T. R. Gilbert, K. D. Onan and M. Veidis, *J. Am. Chem. Soc., 106,* 4596 (1984).
9 G. Davies, M. A. El-Sayed and A. El-Toukhy, *Inorg. Chem., 25,* 2269 (1986).
10 G. Davies; M. A. El-Sayed and A. El-Toukhy, *Inorg. Chem., 25* (1986) in press.
11 L. El-Sayed, M. F. Iskander and A. El-Toukhy, *J. Inorg. Nucl. Chem., 36,* 1739 (1974).
12 P. L. Ganzel, R. A. Sparks and K. N. Trueblood, 'FMLS', anisotropic, full-matrix least-squares refinement, UCLA (modified by A. T. McPhail, Duke University); C. K. Johnson, 'ORTEP', crystallographic illustration program, ORNL-3794, Oak Ridge, Tenn., 1976.
13 D. T. Cromer and J. T. Waber, *Acta Crystallogr., 18,* 104 (1965).
14 'International Tables for X-Ray Crystallography', Vol. 3, Kynoch Press, Birmingham, U.K. 1974.
15 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
16 K. D. Onan, G. Davies, M. A. El-Sayed and A. El-Toukhy, *Inorg. Chim. Acta, 113,* 000 (1986).
17 R. C. Elder, L. R. Florian, R. E. Lake and A. M. Yacynych, *Inorg. Chem., 12,* 2690 (1973).
18 N. Serpone and D. G. Bickley, *Prog. Inorg. Chem., 17,* 391 (1972) and refs. therein.

19 G. A. Lawrence and S. Suvachittanont, *Inorg. Chim. Acta, 32,* L13 (1979).

20 G. Davies, M. A. El-Sayed, A. El-Toukhy, T. R. Gilbert and K. Nabih, *Inorg. Chem., 25,* 1929 (1986); G. Z. Cai, G. Davies, M. A. El-Sayed, A. El-Toukhy and K. D. Ohan, *Inorg. Chem., 25,* 1935 (1986).
T. R. Gilbert, *Inorg. Chem., 25,* 2373 (1986).

21 G. Davies, M. A. El-Sayed, A. El-Toukhy, M. Henary and T. R. Gilbert, *Inorg. Chem., 25,* 2373 (1986).

22 G. Davies, M. A. El-Sayed, A. El-Toukhy, M. Henary, T. S. Kasemans and C. Martin, *Inorg. Chem., 25* (1986) in press.

23 G. Davies, M. A. El-Sayed, A. El-Toukhy and M. Henary, *Inorg. Chem.,* submitted for publication.

24 G. Davies, N. El-Kady, M. A. El-Sayed, A. E.-Toukhy, K. D. Onan and W. Shomaly, *Inorg. Chem.,* submitted for publication.