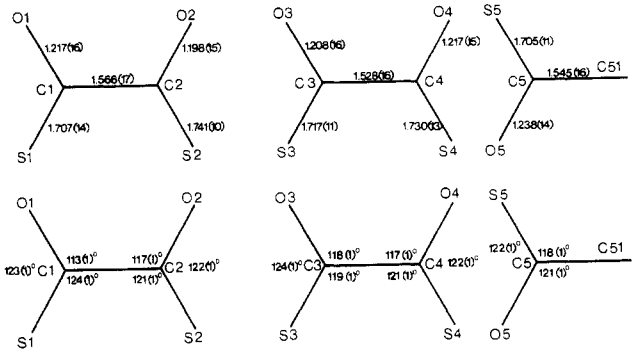


Figure 2. Dimensions and angles within the three different dithiooxalate ligands.

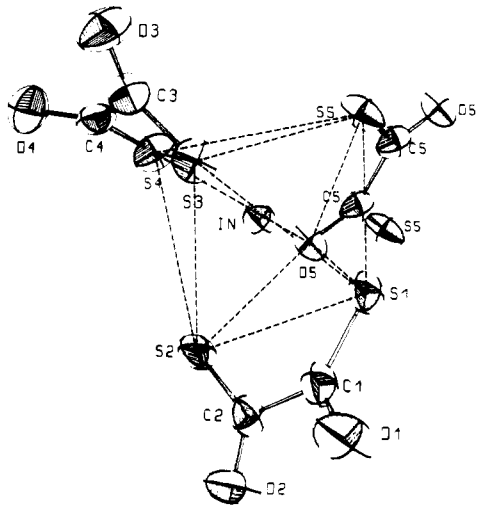


Figure 3. Arrangement of three dithiooxalate ligands around the indium ion causing a distorted octahedral InS_5O polyhedron.

as shown in Figure 1. Interatomic distances and angles of the anion with their estimated standard deviations are listed in Table III and are shown in Figure 2. The numbering scheme of the anion $[(O_2C_2S_2)_2In(SOC_2SO)In(S_2C_2O_2)_2]^{4-}$ is shown in Figures 3 and 4.

Two indium atoms and five dithiooxalate groups form a dimer containing an $In_2S_{10}O_2C_2$ skeleton. Either indium ion is coordinated to two dithiooxalate ligands in cis arrangement. The fifth dithiooxalate acts as a symmetric quadridentate bridging ligand linking both $In(S_2C_2O_2)_2$ units. This ligand represents the first authentic example of a coordinated dithiooxalate in trans arrangement. Thus, the indium atoms are coordinated by five sulfur atoms and one oxygen atom, causing a distorted octahedral coordination sphere as shown in Figure 3. While four In–S distances are practically equal, having an average value of 2.551 (3) Å (see Table III), the fifth sulfur atom, belonging to the bridging ligand, has a longer distance (2.638 (4) Å). This value lies near the average In–S bond length 2.604 (8) Å in the octahedral tris(maleonitriledithiolato)indate(III) trianion, $[In(S_2C_2(CN)_2)_3]^{3-}$, the only other In(III) complex with a 1,2-dithio ligand whose structure has been determined by X-ray analysis.[11] The In–O distance is 2.334 (7) Å. This value is significantly larger than the Sn–O distance to the bridging cis dithiooxalate in the complex $K[Sn[dto(Cu(P(tol)_3)_2)](dto)_2]\cdot 2C_3H_6O$,[4h] which is 2.158 (4) Å. As expected, the angles in the octahedron vary significantly from a minimum value of 74° for O(5)–In–S(5) to a maximum value of 98° for S(3)–In–S(5) (see Table III).

There are three types of dithiooxalate ligands in the molecule. In contrast to the nearly planar bridging trans dithiooxalate containing the inversion center of the whole molecule, the other four terminal ligands deviate more or less from the planarity and can be divided into two groups as to be seen from the torsion angles along the C–C bond. These angles have the values 11° for O(1)–C(1)–C(2)–O(2) and 17° for S(1)–C(1)–C(2)–S(2) in the one ligand type and 41° for O(3)–C(3)–C(4)–O(4) and 49° for S(3)–C(3)–C(4)–S(4) in the other one causing to angles of 15 and 45°, respectively, between the thiocarboxylic units in the ligands. Hitherto, such strong distortions of the coordinated dithiooxalate ligands have not been found in other complexes. Despite of this fact, in all three types of ligands the C–C, C–O, and C–S distances and the S–C–O angles also are similar to those found in some other dithiooxalate compounds.[4d,h,12-15] In the structure there are two different types of tetraphenylarsonium cations whose geometry is tetrahedral, in good agreement with earlier determinations,[16] and is not further discussed.

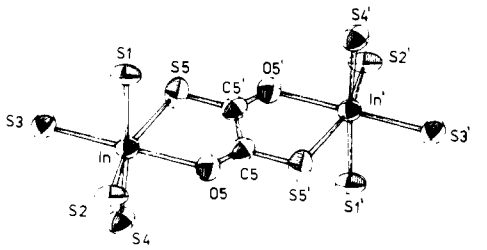


Figure 4. Central part of the anion $[In_2(dto)_5]^{4-}$ with a planar dto bridge in trans arrangement containing the inversion center of the molecule.

The $(Ph_4As)_4[In_2(dto)_5]$ complex shuts a gap because, despite the usually extensive coordination chemistry of indium with dithiolate ligands,[17] surprisingly no indium dithiooxalate complexes have been reported.

Acknowledgment. We thank Professor Dr. J. Šiftar of the University of Ljubljana and Professor Dr. E. Hoyer of the University of Leipzig for helpful discussions. The financial support by the Research Community of Slovenia is also gratefully acknowledged.

Registry No. $(Ph_4As)_4[In_2(dto)_5]$, 79725-63-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (Table IV), atomic coordinates and anisotropic temperature factors of all atoms (Table V), and atomic coordinates of the generated phenyl hydrogen atoms (Table VI) (41 pages). Ordering information is given on any current masthead page.

(11) Einstein, F. W.; Jones, R. D. C. *J. Chem. Soc. A* **1971**, 2762.
(12) Mattes, R.; Meschede, W.; Stork, W. *Chem. Ber.* **1975**, *108*, 1.
(13) Maury, F.; Gleizes, A. *Inorg. Chim. Acta* **1980**, *41*, 185.
(14) Butler, K. R.; Snow, M. R. *Acta Crystallogr., Sect. B* **1975**, *B31*, 345.
(15) Mennemann, K.% Mattes, R. *J. Chem. Res., Miniprint* **1979**, 1340, 1369.
(16) Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1976**, *15*, 1589.
(17) Carty, A. J.; Tuck, D. G. *Prog. Inorg. Chem.* **1975**, *19*, 243.

Contribution from the Departments of Chemistry, Portland State University, Portland, Oregon 97207, and the Oregon Graduate Center, Beaverton, Oregon 97006

Chromium Oxide Trifluoride ($CrOF_3$). Preparation and Properties

P. J. Green,[1a] B. M. Johnson,[1a] T. M. Loehr,[1b] and G. L. Gard*[1a]

Received January 5, 1982

Chromium trioxide reacts with chlorine monofluoride at 0 °C to produce chromyl fluoride.[2a] When the interaction of

 © 1982 American Chemical Society

Table I. Vibrational Frequencies of Solid $CrOF_3$ (cm^{-1})

IR	Raman	IR	Raman
1000 s	1000 s	480 m	473 m
785 w	789 w		450 m
718 s	714 m, b (740 sh)	380 w	395 s
682 s	690 m	350 vw	354 s (337 sh)
600 vs	607 w		291 s
565 s	562 vw	270 m	269 m
512 s	527 m		190 s

ClF and CrO_3 at higher temperatures was studied, it was found that the amount of CrO_2F_2 produced decreases with increasing reaction temperature, while the yield of a nonvolatile brick red solid increased to 100% at 100 °C. This solid displayed properties similar to the products reported from the reactions of ClF_3, BrF_3, or BrF_5 with CrO_3.[2b,3] These products were found to be reddish solids with the following composition: $CrOF_3 \cdot 0.30ClF_3$, $CrOF_3 \cdot 0.25BrF_3$, and $CrOF_3 \cdot 0.25BrF_5$. Attempts to remove these interhalogens resulted in only decomposition and failed to produce $CrOF_3$. Interestingly, potassium dichromate was found to react with BrF_3, forming $KCrOF_4 \cdot 0.5BrF_3$, which can be transformed to $KCrOF_4$ upon heating under vacuum.[4]

We have found that brick red solid formed from the reaction of ClF and CrO_3 or CrO_2F_2 to have a composition that varies from $CrOF_3 \cdot 0.10ClF$ to $CrOF_3 \cdot 0.21ClF$. However, multiple treatments of this product with fluorine at 120 °C produced a bright purple solid, which was found to be chromium oxide trifluoride ($CrOF_3$).

Purple $CrOF_3$ is only midly hygroscopic, hydrolyzing in water to a yellow-green solution due to the disproportionation reaction

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \quad (1)$$

On the basis of the above equation, a standard iodometric determination gave an apparent Cr(VI) value of 27.6% (theoretical 27.7%). Total chromium was found iodometrically, after oxidizing the hydrolyzed sample with sodium peroxide, as 41.6% (theoretical 41.6%). $CrOF_3$ slowly attacks glass above 230 °C; this attack becomes extensive at 300 °C and is accompanied by apparent melting. $CrOF_3$ reacts vigorously with acetone, hexane, and $(CH_3)_2SO$, but is insoluble in CCl_4, C_7F_{16}, and $ClCF_2CF_2Cl$. Preliminary work suggests that $CrOF_3$ is slightly soluble in anhydrous HF and BrF_3. The magnetic susceptibility of even the ClF-contaminated $CrOF_3$ product (at 17 °C) yielded a value of 1.82 μ_B, consistent with that of a d^1 Cr(V) species.

Heating $CrOF_3$ to 500 °C produced the decomposition

$$CrOF_3 \xrightarrow{\Delta} CrF_3 + {}^1/_2O_2 \quad (2)$$

and heating with F_2 at 190 °C produced CrF_5:

$$CrOF_3 + F_2 \xrightarrow{\Delta} CrF_5 + {}^1/_2O_2 \quad (3)$$

In anhydrous HF, KF and $CrOF_3$ produced the salt $KCrOF_4$:

$$CrOF_3 + KF \xrightarrow{HF} KCrOF_4 \quad (4)$$

The infrared (IR) and Raman (R) spectra of $CrOF_3$ are presented in Figures 1 and 2 and tabulated in Table I. The strong band at 1000 cm^{-1} can be unambiguously assigned to a terminal chromium–oxygen stretch; for solid VOF_3[5] and solid $MoOF_3$[6] the ν(M=O) terminal stretching frequency was found at 1039 (R) and 1000 (IR) cm^{-1}, respectively. The bands in the 600–740-cm^{-1} region are attributed to the ν(Cr–F) terminal stretching modes; for VOF_3[5] the strong band found at 741 (R) cm^{-1} was tentatively assigned to a terminal fluorine stretching mode; for NbF_5 and TaF_5 the strong IR bands in the 689–749-cm^{-1} region were attributed to M–F stretching modes.[7] It is thought that the absorption band at 565 cm^{-1} (and the very weak Raman band at 562 cm^{-1}) is due to a bridging fluorine stretching mode, ν(Cr–F–Cr). In solid chromyl fluoride the Raman band at 540 cm^{-1} was attributed to a fluorine bridge structure;[8] with $ReOF_4$ in its powder form an infrared absorption band at 540 cm^{-1} was tentatively assigned to a bridge fluorine mode;[9] however, since for NbF_5 and TaF_5 the bridging mode was located at 541 and 479 cm^{-1}, respectively, it is possible that in $CrOF_3$ the IR bands at 412 or 480 cm^{-1} may also be due to a bridging fluorine system.

Most of the low-frequency bands (450–269 cm^{-1}) cannot be readily assigned. These low-frequency vibrations probably arise principally from various Cr–F and Cr–O deformation modes.[8]

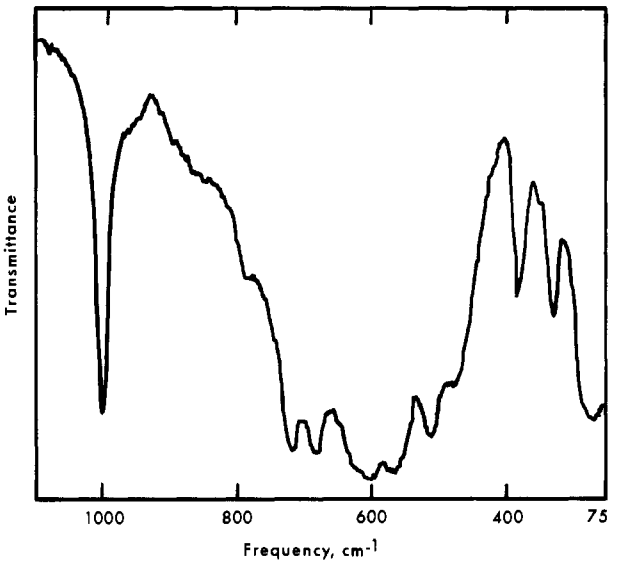


Figure 1. Infrared spectrum of solid chromium oxide trifluoride, $CrOF_3$.

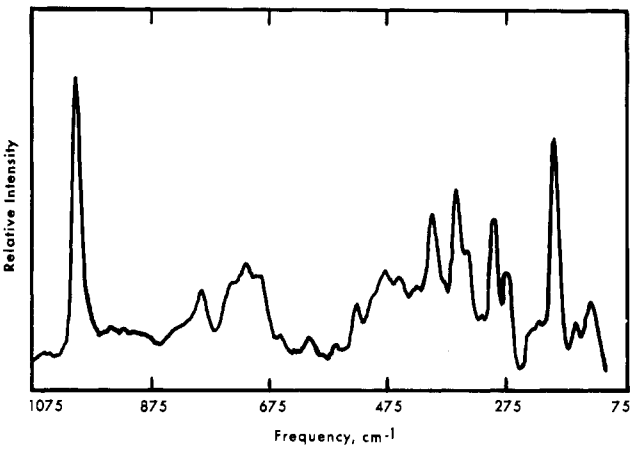
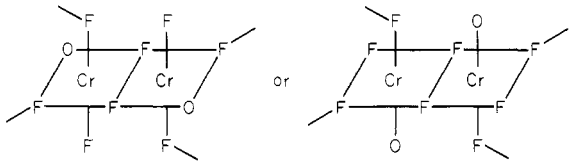


Figure 2. Raman spectrum of solid chromium oxide trifluoride, $CrOF_3$.

(1) (a) Portland State University. (b) Oregon Graduate Center.
(2) (a) P. J. Green and G. L. Gard, *Inorg. Chem.*, **16**, 1243 (1977). (b) H. C. Clark and Y. N. Sadana, *Can. J. Chem.*, **42**, 50 (1964).
(3) H. C. Clark and Y. N. Sadana, *Can. J. Chem.*, **42**, 702 (1964).
(4) A. G. Sharpe and A. A. Woolf, *J. Chem. Soc.*, 798 (1951).
(5) I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc. A*, 1210 (1970).
(6) G. E. Blokhina, I. N. Belyaev, A. Opalovskii, and L. I. Belan, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **17**, 1113 (1972).
(7) L. E. Alexander, I. R. Beattie, and P. J. Jones, *J. Chem. Soc., Dalton Trans.*, 210 (1972).
(8) S. D. Brown, G. L. Gard, and T. M. Loehr, *J. Chem. Phys.*, **64**, 1219 (1976).
(9) R. T. Paine, K. L. Treuil, and F. E. Stafford, *Spectrochim. Acta, Part A*, **29A**, 1891 (1973).

It appears that $CrOF_3$, like $CrOCl_3$,[10] $MoOCl_3$,[11] and VOF_3, is a polymeric solid with terminal Cr–O bonds and extensive halide bridging. A proposed tentative structure is given by **1**. This suggested polymeric structure of $CrOF_3$ also accounts for the lack of volatility and solubility in various solvents.



1

The infrared spectrum of $KCrOF_4$ contains the M=O terminal stretching at 1020 cm^{-1}. In $CsVOF_4$[12] the V–O stretching frequencies were found at 1016 and 1023 cm^{-1}. The Cr–F stretching frequencies are located within the broad 640-cm^{-1} region; it is possible that the absorption band at 500 cm^{-1} is due to fluorine bridging. These data suggest (as with $CsVOF_4$) a C_{4v} symmetry with the MOF_4^- ion as being essentially monomeric with possible fluorine bridging. The assumption of C_{4v} symmetry for $CrOF_4^-$ is reasonable as this structure has been assumed for many $CrOCl_4^-$ salts and has been confirmed for $[AsPh_4][CrOCl_4]$.[13] An X-ray powder pattern of $KCrOF_4$ was obtained; it correlated closely with a pattern calculated from the unit cell constant data of Clark and Sadana.[3] Lines attributable to KF or $CrOF_3$ were not present.

Although we have formulated the brick red solid formed from CrO_3 and ClF as a ClF adduct of $CrOF_3$, the exact nature of this material is not well understood. The formation of only ClO_2F upon fluorination suggests that the adduct contains ClO_2F instead of ClF. Further studies of $CrOF_3$ are planned. The presence of O_2 in the fluorine reagent may account for these observations.

Experimental Section

Chromyl fluorinde was prepared via reaction of ClF and CrO_3 at 0 °C and stored over NaF at room temperature before use.[2a] Chlorine monofluoride (Ozark-Mahoning) was used as received. Fluorine (Air Products, 98%) was handled in a well-passivated copper line. Chromium trioxide and potassium fluoride (Baker, reagent grade) were dried prior to use.

Infrared (IR) spectra were obtained either neat between KRS-5 plates or as KBr pellets and recorded on a Perkin-Elmer 467 (IR) spectrometer. Spectra of gases were taken with use of a Monel cell (path length 8.25 cm) fitted with either AgCl or KRS-5 windows. All IR spectra were calibrated with polystyrene film. Raman (R) spectra were obtained with a Jarrell-Ash 25-300 Raman spectrometer equipped with a Spectra-Physics 164 krypton ion laser for excitation at 647.1 and 568.2 nm. The scattered radiation was detected at approximately 180° geometry with a thermoelectrically cooled FW-130(S-20) photomultiplier tube, photon-counting electronics, and repetitive scanning. Samples were sealed in 4-mm Pyrex glass tubing.

The X-ray powder spectra were obtained with an XRD-5 General Electric camera. Samples were contained in 0.5-mm Lindemann glass capillaries. Nickel-filtered Cu Kα radiation was used. The procedure was standardized with known compounds (CrO_3, Cr_2O_3) for which the calculated *d* values agreed with the published ASTM values.

Magnetic susceptibility was measured with use of the Gouy method. Measurements were made at a field strength of about 5 kg with an Alfa A1 7500 water-cooled magnet with a 3.8-cm air gap. Mercury(II) tetrakis(thiocyanato)cobaltate(II) was used for calibration. Diamagnetic corrections were applied with use of Pascal's constants.

Elemental analyses were performed by Beller Laboratories, Göttingen, West Germany.

Preparation of $CrOF_3$ from CrO_3. To 35 mmol of predried CrO_3 in a passivated 100-mL Monel vessel equipped with nickel helices and a Hoke stainless steel valve was added 151 mmol of ClF. The reaction mixture was heated at 110 °C for 4 h with periodic shaking, after which time the vessel was evacuated at −196 °C, −78 °C, and room temperature. The −196 °C volatile product was found to be oxygen as identified by its molecular weight (theoretical 32.0, found 31.7); at −78 °C the volatile materials consisted of ClF and ClO_2F, identified by their respective infrared spectra, and Cl_2, identified as a yellow-green liquid at −78 °C with a vapor pressure of ca. 100 torr at that temperature. No volatile materials were found at 20 °C, and the weight of the solid (4.57 g) corresponded to the empirical composition $CrOF_3 \cdot 0.10ClF$.

The reaction vessel containing the chlorine-containing compound was charged with 5.0 mmol of F_2 and heated to 120 °C for 12 h. Removal of the excess fluorine at −196 °C left behind at room temperature a gas (4.9 mmol of ClO_2F) and a solid. After the ClO_2F was removed, the vessel was charged again with 5.0 mmol of F_2 and heated to 120 °C for 2 h. The volatile materials were again removed (0.35 mmol of ClO_2F), and the solid was again treated with a new charge of F_2 (5.0 mmol) and heated at 120 °C for 3 h. Removal of all volatile materials (0.03 mmol of ClO_2F) left behind a bright purple solid (34 mmol of $CrOF_3$) that was obtained in 97% yield. The X-ray powder spectrum gave the following *d* values (in Å) with their respective intensities: 4.96 (m), 4.46 (s), 4.04 (m), 3.76 (s), 3.64 (s), 3.37 (vs), 2.83 (w), 2.75 (vw), 2.58 (m), 2.48 (s), 2.24 (s), 2.04 (m), 2.01 (w), 1.95 (w), 1.89 (w), 1.86 (vw), 1.82 (m), 1.69 (m), 1.50 (s), 1.53 (w), 1.49 (w), 1.46 (vw), 1.43 (m), 1.41 (m), 1.20 (m).

Anal. Calcd for $CrOF_3$: Cr, 41.60; F, 45.6. Found: Cr, 41.72; F, 45.4.

Preparation of $CrOF_3$ from CrO_2F_2. To 14 mmol of CrO_2F_2 in a passivated 100-mL Monel vessel equipped with nickel helices and a Hoke stainless steel valve was added 35 mmol of ClF. The reaction mixture was heated to 100 °C for 12 h, after which time the vessel was evacuated at −196 °C, −78 °C, and room temperature. The −196 °C product was found to be oxygen (theoretical molecular weight 32.0, found 31.9); the −78 °C fraction consisted of ClF and ClO_2F, identified by their respective infrared spectra, and Cl_2, identified as a yellow-green liquid at −78 °C with a vapor pressure of ca. 100 torr at that temperature. No volatile materials were found at room temperature. The brick red, nonvolatile solid (1.86 g) corresponded to the empirical composition $CrOF_3 \cdot 0.14ClF$. Treatment of the above product (16 mmol) with fluorine (20 mmol) at 120 °C (4 h) produced a purple solid whose properties and X-ray powder and infrared spectra essentially agreed with those found for $CrOF_3$ produced from CrO_3.

Decomposition of $CrOF_3$. To a passivated 100-mL Monel vessel was added 33 mmol of $CrOF_3$. A light green solid (34 mmol of CrF_3) and a gas (16 mmol of O_2; theoretical molecular weight 32.0, found 32.2) were formed upon heating to 500 °C (5 h). The X-ray powder spectrum agreed with that reported for CrF_3.

Anal. Calcd for CrF_3: Cr, 47.7; F, 52.3. Found: Cr, 44.7; F, 48.4.

Fluorination of $CrOF_3$. To 40 mmol of $CrOF_3$ in a 100-mL Monel vessel equipped with a Hoke stainless steel valve was added 71 mmol of F_2. The reaction mixture was heated at 190 °C for 15 h. removal of volatile materials at room temperature left behind a deep red solid which fumed in air, hydrolyzed to a yellow-green solution, and ignited acetone. An infrared spectrum showed the solid to be CrF_5 (35 mmol), which was produced in 88% yield.

Preparation of $KCrOF_4$. To 26 mmol of $CrOF_3$, 26 mmol of KF was added in a 40-mL Kel-F vessel equipped with a Teflon-covered stirring bar, a Teflon top, and Whitney stainless steel valve. Anhydrous HF (710 mmol) was vacuum distilled into the vessel at −196 °C. A deep purple solution was formed upon warming to room temperature, while it was magnetically stirred for 1 h. The volatile materials at 40 °C were pumped away through a trap cooled to −196 °C. The product left behind retained 25 mmol of HF. Heating this product at 100 °C for 1 h left behind a tan-green solid (26 mmol of $KCrOF_4$) which darkened in moist air and hydrolyzed to a yellow solution and a green solid. Its infrared spectrum contained the following bands (cm^{-1}): 1020 (s), 962 (m), 640 (vs, b), 500 (s), 350 (m), 285 (m). The X-ray powder spectrum gave the following *d* values (in Å) with their respective intensities: 8.12 (m), 5.56 (s), 5.17 (s), 4.90 (m), 4.70 (m), 4.37 (m), 4.21 (s), 4.06 (w), 3.97 (w), 3.51 (w), 3.46 (w), 3.35 (s), 3.29 (s), 3.23 (s), 2.70 (w), 2.64 (w), 2.58 (w), 2.38 (w), 2.35 (w), 2.33 (w), 2.30 (w), 2.21 (m), 2.16 (m), 1.91 (m), 1.87 (w).

(10) W. Levason, J. S. Ogden, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 419 (1980).
(11) M. G. B. Drew and I. B. Tomkins, *J. Chem. Soc. A*, 22 (1970).
(12) J. A. S. Howell and K. C. Moss, *J. Chem. Soc. A*, 270 (1971).
(13) C. D. Garner, J. Kendrick, P. Lambert, F. E. Mabbs, and I. H. Hillier, *Inorg. Chem.*, **15**, 1287 (1976).

Anal. Calcd for $KCrOF_4$: Cr, 28.40; F, 41.5. Found: Cr, 28.26; F, 42.5.

Acknowledgment. We wish to acknowledge gratefully the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $CrOF_3$, 43997-25-7; CrO_3, 1333-82-0; CrO_2F_2, 7788-96-7; $KCrOF_4$, 68258-60-6; CrF_5, 14884-42-5; ClF, 7790-89-8; KF, 7789-23-3.

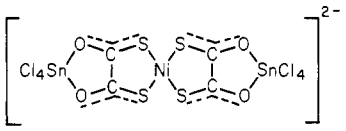
Contribution from the Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Electron Spin Resonance Spectra of the One-Electron-Reduction Products of Stannic Chloride Adducts of Bis(dithiooxalato)nickelate(II), -palladate(II), and -platinate(II) Complexes

G. A. Bowmaker, P. D. W. Boyd,* and G. K. Campbell

Received January 5, 1982

Stannic chloride forms 1:1 and 1:2 adducts with bis(dithiooxalato)nickel(II) and bis(dithiooxalato)palladium(II) anionic complexes, $[M(S_2C_2O_2)_2]^{2-}$, M = Ni, Pd, and a crystal structure determination for the 1:2 adduct of the nickel complex (I) showed that the $SnCl_4$ molecules are coordinated to



I

the α-diketone oxygen atoms of the dithiooxalate ligands, which are themselves S-bonded to nickel as in the parent bis(dithiooxalato) complex. The coordination about Ni is square planar and that about Sn is octahedral.[1,2]

Unlike the parent bis(dithiooxalato)metalate complexes, the $SnCl_4$ adducts undergo well-defined reversible electrochemical reductions. The 1:1 adducts undergo a single reversible one-electron reduction while the 2:1 adducts undergo reversible reduction in two one-electron steps. It has been suggested that these reductions are ligand rather than transition metal based, the added electrons going into a ligand π-antibonding orbital whose energy is lowered relative to that in the parent bis(dithiooxalate) complex by adduct formation with $SnCl_4$.[1,2]

In the course of our work on the spectroelectrochemistry of nickel(II) complexes with sulfur ligands,[3] we have measured the ESR spectra of the one-electron-reduction products of the complexes described above by in situ electrolysis. We have also studied the electrochemical reduction of the 1:1 and 1:2 $SnCl_4$ adducts of the bis(dithiooxalato)platinum(II) dianion, $[Pt(S_2C_2O_2)_2]^{2-}$, and have measured the ESR spectra of the one-electron-reduction products. We have also examined the cyclic voltammetry of the parent $[M(S_2C_2O_2)_2]^{2-}$ complexes for comparison with the previously published results for the $SnCl_4$ adducts.

Experimental Section

Preparation of Compounds. Bis(tetraphenylphosphonium) Bis(dithiooxalato)metalates(II). These were prepared in a manner similar to that described previously by Coucouvanis et al.[1,2] for the corresponding bis(benzyltriphenylphosphonium) salts, with the exception that the products were recrystallized from nitromethane/diethyl ether instead of dimethylformamide/ether. The compounds were obtained as the 1:1 nitromethane solvates (M = Ni, Pd) or as the 2:1 nitromethane solvate (M = Pt). This was verified by ^1H NMR and elemental analysis. $[Ph_4P]_2[Ni(S_2C_2O_2)_2]\cdot CH_3NO_2$: mp 285 °C. Anal. Calcd for $C_{53}H_{43}NNiO_6P_2S_4$: C, 61.27; H, 4.17. Found: C, 61.56; H, 4.78. $[Ph_4P]_2[Pd(S_2C_2O_2)_2]\cdot CH_3NO_2$: mp 227 °C. Anal. Calcd for $C_{53}H_{43}NP_6P_2PdS_4$: C, 58.58; H, 3.99. Found: C, 58.35; H, 4.43. $[Ph_4P]_2[Pt(S_2C_2O_2)_2]\cdot 2CH_3NO_2$: mp 219 °C. Anal. Calcd for $C_{54}H_{46}N_2O_8P_2PtS_4$: C, 52.46; H, 3.75. Found: C, 52.50; H, 4.35.

Stannic Chloride Adducts. Attempts were made to prepare these by the method described by Coucouvanis et al. for the corresponding bis(benzyltriphenylphosphonium) salts. A pure product was obtained only in the case of the 1:1 adduct with the bis(dithiooxalato)nickelate(II) complex. $[Ph_4P]_2(Ni(S_2C_2O_2)_2(SnCl_4)]$: mp 204 °C. Anal. Calcd for $C_{52}H_{40}Cl_4NiO_4P_2S_4Sn$: C, 50.44; H, 3.26. Found: C, 50.36; H, 3.61. In all other cases addition of $SnCl_4$ to a CH_2Cl_2 solution of the bis(dithiooxalato)metalate(II) complex in a 1:1 or 2:1 mole ratio produced an immediate color change, indicating that adduct formation had taken place, but attempts to crystallize these adducts by addition of pentane resulted only in oils, which could not be recrystallized from common solvents. The formation of the 1:1 and 1:2 adducts was verified by cyclic voltammetry of solutions of the bis(dithiooxalato)metalate(II) complex and $SnCl_4$ in appropriate mole ratios in $CHCl_2$ and by the ESR spectra of the one-electron-reduction products (see Results and Discussion).

Electrochemistry. Electrochemical measurements were carried out at a platinum electrode by using a PAR 173 potentiostat with a PAR 179 digital coulometer with IR compensation, an ECG 175 universal programmer, and an HP 7046A X-Y recorder. The reference electrode was Ag/AgCl (0.1 M LiCl in CH_2Cl_2) separated from the voltammetric cell by a 0.1 M $[Bu_4N]ClO_4$ in CH_2Cl_2 salt bridge. Measurements were carried out in dichloromethane (0.1 M $[Bu_4N]ClO_4$ supporting electrolyte) or in acetonitrile (0.1 M $[Bu_4N]ClO_4$ supporting electrolyte). All potentials were internally referenced to the potential for the one-electron oxidation of ferrocene (+0.46 V vs. Ag/AgCl) or the one-electron oxidation of $[Pt((CN)_2C_2S_2)_2]^{2-}$ (+0.16 V vs. Ag/AgCl) as described previously.[3]

Electron Spin Resonance Spectra. X-band electron spin resonance spectra were recorded with a Varian E4 spectrometer. The electrochemically produced species were generated in situ on a platinum electrode by controlled-potential electrolysis using a three-electrode configuration,[3] at potentials slightly beyond the measured redox potential of the complex. Electrolyses in this cell could be carried out at ambient or lower temperatures with use of the Varian variable-temperature attachment. Frozen-solution spectra were obtained by freezing the contents of the in situ cell after electrolysis.

The method used to simulate frozen-solution spectra has been described previously.[3]

Results and Discussion

(a) Ni and Pd Complexes. The only $SnCl_4$ adduct of the bis(tetraphenylphosphonium) bis(dithiooxalato)metalate(II) complexes that could be obtained in pure crystalline form is the 1:1 adduct $[Ph_4P]_2[Ni(S_2C_2O_2)_2SnCl_4]$. However, it is clear from the cyclic voltammetry of CH_2Cl_2 solutions containing the parent bis(dithiooxalato)metalate(II) complexes and $SnCl_4$ in the appropriate mole ratios, that the 1:1 and 1:2 adducts are readily formed in solution. The cyclic voltammetric parameters for the adducts are given in Table I. The $E_{1/2}$ values are all about 0.4 V more positive than those reported previously for the corresponding bis(benzyltriphenylphosphonium) salts, but this difference is probably due to the different reference systems used for measuring the potentials (see Experimental Section). The relative $E_{1/2}$ values between different complexes and between different waves in the same complex in the case of the 1:2 adducts agree well with those found previously for the corresponding bis(benzyltriphenylphosphonium) salts.[1,2]

Electrolysis of solutions of the $SnCl_4$ adducts in the in situ cell at room temperature at potentials corresponding to the first one-electron-reduction step produced strong ESR signals. Representative spectra are shown in Figures 1 and 2, and the ESR parameters are listed in Table II.

(1) Coucouvanis, D. *J. Am. Chem. Soc.* **1970**, *92*, 707.
(2) Coucouvanis, D.; Baenziger, N. C.; Johnson, S. M. *J. Am. Chem. Soc.* **1973**, *95*, 3875.
(3) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K.; Hope, J. M.; Martin, R. L. *Inorg. Chem.* **1982**, *21*, 1152. Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. *Ibid.* **1982**, *21*, 2403.

0020-1669/82/1321-3565$01.25/0 © 1982 American Chemical Society