Journal of Fluorine Chemistry, 52 (1991) 13–27

FLUOROSULFATE DERIVATIVES OF DIVALENT GOLD

H. WILLNER*, F. MISTRY, G. HWANG, F. G. HERRING, M. S. R. CADER,
and F. AUBKE**

Department of Chemistry, The University of British Columbia, Vancouver, B.C.,
V6T 1Y6 (Canada)

SUMMARY

The reduction of gold(III) fluorosulfate, $Au(SO_3F)_3$ with either gold powder or carbon monoxide, in fluorosulfuric acid, HSO_3F, yields gold(II) fluorosulfate as a yellow-red solid in high yield. Based on magnetic measurements and vibrational spectra, formulation as mixed valency Au(I) Au(III)-$(SO_3F)_4$ is suggested. Evidence from ESR measurements for a solvated, paramagnetic Au(II)-species in the supernatant solution is obtained and discussed.

INTRODUCTION

In binary compounds and complexes gold preferentially exhibits the oxidation state +3 and square planar coordination for the metal [1]. Only in

---

* Present address: Institut für Anorganische Chemie der Universität, Callinstr. 9, D-3000 Hannover, F.R.G.

** Author to whom correspondence should be addressed.

0022-1139/91/$3.50

compounds with fluorine, oxidation state +5 and octahedral coordination are encountered [1] [2]. For the heavier halogens, univalent compounds of the type AuX with X = Cl, Br or I are found to be chain polymers [1]. Here and in anionic complexes of the type $[AuX_2]^-$ (X = Cl, Br, I or a pseudohalogen), linearly coordinated gold is present [1]. Binary compounds with gold in an even oxidation state (+2 or +4) are extremely uncommon [1] [2].

Gold(II) chloride appears to be an apparent exception to this straightforward situation. However the compound is diamagnetic, and according to its cyclic, molecular structure [3], is better viewed as a mixed valency compound of the composition Au_4Cl_8 with square planar coordination for Au(III) and linear coordination for Au(I). The compound appears to be the best characterised example of a very small group of mixed valency Au(I)-Au(III) compounds [1]. Tervalent gold and square planar coordination are also found in gold(III) fluorosulfato compounds [4] [5], as evidenced by a recent crystal structure study of $Au(SO_3F)_3$ [6]. Like the fluorides, where both AuF and AuF_2 are unknown [2], examples for lower valent fluorosulfates of gold are so far lacking.

A very recent report [7] on the interaction of carbon monoxide gas at room temperature and atmospheric pressure with a solution of $Au(SO_3F)_3$ in fluorosulfuric acid, resulting ultimately in the formation of gold(I) monocarbonylato fluorsulfate, $Au(CO)SO_3F$, has indicated that gold(III) may be reduced under mild conditions, in HSO_3F [8] as reaction medium.

We want to report here on the reduction of gold(III) fluorosulfate with CO or gold powder in HSO_3F, yielding two novel and interesting results:

(i) the formation, isolation and characterisation of gold(II) fluorosulfate, $Au(SO_3F)_2$, and

(ii) the detection of a solvated Au^{2+} species by electron spin resonance spectroscopy (ESR) in the supernatant solution.

EXPERIMENTAL

Chemicals

Gold powder, - 20 mesh of 99.95% purity was obtained from the Ventron Corporation (Alfa Inorganics). Bis(fluorosulfuryl)peroxide, $S_2O_6F_2$ [9], and gold(III) fluorosulfate [5] were synthesized, and technical grade fluorosulfuric acid (Orange County Chemicals) [10] was purified according to published methods.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 598 grating spectrometer. Solid samples were pressed as thin films between KBr, AgCl and AgBr (Harshaw Chemicals). A Raman spectrum of solid $Au(SO_3F)_2$ was recorded on a Bruker Fourier Raman Spectrometer FRA 106 by Dr. Sawatzki, Bruker Analytische Messtechnik, Karlsruhe, F.R.G. ESR spectra were recorded at 80 and 298 K on an X-band homodyne spectrometer with a Varian 12-inch magnet, equipped with a MKII Field Dial control and a Varian E-257 temperature controller. Further details on the ESR spectrometer and the simulation programme have been described recently [11]. A Princeton Applied Research model 155 vibrating sample magnetometer was used to obtain magnetic susceptibilities. Details on the instrument have been published previously [12].

Solid samples were manipulated inside a Vacuum Atmosphere Corp. Dri-Lab, model HE-493 filled with dry N_2 and equipped with a HE-493 Dri-Train. Standard vacuum line techniques were employed for the manipulation of volatile compounds. Some of the reactions were performed in sealed off all-glass ampuls. The ampul was opened in vacuum, using an 'ampul key' as described previously [13]. In addition Pyrex reaction vials of 120 mm length and 10 mm o.d. fitted with Young valves were used on occasion. An apparatus as described by Shriver [14] was used for the filtration of the moisture sensitive reaction mixture. Chemical analyses were performed by Mr. P. Borda of this

Department. Gold content was determined by pyrolysis of a known amount of sample at ~900°C in a stream of O_2, with gold the sole residue.

Synthetic Reaction

To a freshly prepared solution of 499 mg (1.02 mmol) of $Au(SO_3F)_3$ in about 2 g of HSO_3F, 100 mg (0.508 mmol) of gold powder was added inside a drybox. After addition, the color of the solution changed quickly from yellow-orange to dark-red and later to almost black. A brown precipitate wa observed even before all gold powder was consumed. The reaction mixture was kept at room temperature for 22 days and frequently shaken during this time. After all gold powder appeared to have been consumed, about 0.6 g of the supernatant liquid were removed inside the drybox and used in part for ESR measurements. Removal of all HSO_3F from this liquid fraction yielded about 0.11 g of a black oily substance. Solvent removal from the solid residue formed during the reaction gave 480 mg (1.215 mmol) of a red-yellow solid which analyzed as $Au(SO_3F)_2$. The isolated yield was 79.5%. The solid product was moisture sensitive and did not melt or decompose below 290°C. Analysis: Calc. for $Au(SO_3F)_2$, Au, 49.85%, S, 16.23%. Found: Au, 49.50%, S, 15.78%.

RESULTS AND DISCUSSION

Three closely related aspects of this study will be discussed:

(i) The synthesis of gold(II) fluorosulfate together with possible alternate routes;

(ii) The identification and characterisation of gold(II) fluorosulfate as a mixed valency Au(I)-Au(III) compound; and

(iii) The ESR study of the gold species solvated in fluorosulfuric acid, obtained in the reduction.

The method described in the experimental section, the reduction of gold(III) fluorosulfate by a stoichiometric amount of gold powder in fluorosulfuric acid, proceeds smoothly at room temperature with a reaction time of 22 days according to:

$$2Au(SO_3F)_3 + Au \xrightarrow[HSO_3F]{25°C,\ 22d} 3\ Au(SO_3F)_2 \qquad (1)$$

A considerably faster reduction occurs when the reaction temperature is raised to 65°C and a slight excess of gold(III) fluorosulfate is used. Under these conditions all gold is consumed within 24 hours, resulting in a clear, deep red solution. Over a period of 3 days, with the reactor at room temperature, a red-yellow precipitate of $Au(SO_3F)_2$ forms and is isolated by filtration. The color of the solution remains dark red.

It appears from these observations that solid $Au(SO_3F)_2$ is neither the primary nor the sole reaction product. Attempts to follow the reaction at 25°C by weighing, suggest an isolated yield of just below 80%, with about 20% of the gold presumably present in solution. It is also possible that gold(II) fluorosulfate is somewhat soluble in HSO_3F, with the species present in solution possibly solvated Au^{2+}. In addition to the above route, the reduction of gold(III) fluorosulfate in HSO_3F with gaseous CO produces $Au(SO_3F)_2$ as a byproduct, when the amount of CO used is insufficient to ensure quantitative formation of $Au(CO)SO_3F$ [7]. Separation of both solid products is achieved by sublimation in vacuo: $Au(CO)SO_3F$ sublimes between 70 and 80°C, while $Au(SO_3F)_2$ is nonvolatile under these conditions.

This alternative route to gold(II) fluorosulfate has a closely related precedent in the synthesis of Au_4Cl_8 [3b]. Here, reduction of $AuCl_3$, dissolved in thionyl chloride, $SOCl_2$, is accomplished by CO, and formation of Au(CO)Cl is avoided by strictly maintaining a $AuCl_3$: CO ratio of 1:1 [3b].

Both procedures discussed so far have the use of fluorosulfuric acid in common, and three distinct advantages arise from its use:

(i) HSO_3F is reportedly inert towards gold metal [15] and will not dissolve detectable quantities of CO or react with CO.

(ii) The solubility of $Au(SO_3F)_3$ in the acid is high. This is probably a consequence of the dimeric molecular structure of $Au(SO_3F)_3$ [6], and

(iii) observations made in connection with the synthesis and characterisation of $Au(CO)SO_3F$ [7] strongly suggest, that gold(I) fluorosulfate disproportionates in fluorosulfuric acid according to:

$$3AuSO_3F_{(solv.)} \rightleftharpoons 2Au_{(s)} + Au(SO_3F)_{3(solv.)} \qquad (2)$$

Reactions of this type are reported for gold(I) halides, and the non-existence of AuF is attributed to disproportionation [16].

All three factors contribute to a fast, efficient reaction and to the absence of side reactions, which would result in impure products.

Less useful is the controlled pyrolysis of solid gold(III) fluorosulfate according to:

$$2Au(SO_3F)_3 \xrightarrow{\Delta} 2Au(SO_3F)_2 + S_2O_6F_2 \qquad (3)$$

Even though $S_2O_6F_2$ is formed [17] above 130°C, no stoichiometrically well defined solid products result according to a thermogravimetric study. Evidently $Au(SO_3F)_3$ behaves differently from $Pd(II)Pd(IV)(SO_3F)_6$ [18] and $Ag(SO_3F)_2$ [19] where $Pd(SO_3F)_2$ and $AgSO_3F$ respectively form quantitatively together with $S_2O_6F_2$ on heating.

In summary, it appears that the reduction of gold(III) fluorosulfate with gold powder at room temperature or at 65°C is the most convenient and direct route to gold(II) fluorosulfate, and that fluorosulfuric acid plays an important role in the reduction process.

A comparison to the formally related metal fluorosulfates $Cu(SO_3F)_2$ [20] [21] and $Ag(SO_3F)_2$ [19] is helpful in order to reach structural conclusions regarding the new gold(II) fluorosulfate. The magnetic properties of the three compounds provide a striking difference. As is expected for compounds of ions with a d^9 electron configuration, both $Cu(SO_3F)_2$ and $Ag(SO_3F)_2$ are paramagnetic with reported μ_{eff}^{298} values between 1.91 and 2.08 μ_B[19]-[21]. Their magnetic susceptibilities follow the Curie-Weiss law for the most part, but $Ag(SO_3F)_2$ shows ferromagnetic coupling at about 40K [22]. Gold(II) fluorosulfate on the other hand is diamagnetic with $\chi_M = -107 \times 10^{-6} cm^3 mol^{-1}$ and no ESR signal of the solid is observed at 80 or 298K. Hence, a discrete Au^{2+} ion cannot be present, and a poly-nuclear compound is suggested.

Not surprisingly the vibrational spectra are also distinctly different for both sets of metal(II) fluorosulfates. For $Ag(SO_3F)_2$ [19] and $Cu(SO_3F)_2$ [20][21] like for most $M(SO_3F)_2$ compounds [23], relatively simple IR spectra are obtained. The fluorosulfate group functions as a tridentate oxygen donor ligand, resulting in layer structures of the $CdCl_2$ type [23]. Some observed band splitting [19]-[21] is attributed to Jahn-Teller distortions and the resulting non-octahedral coordination geometries around Cu^{2+} and Ag^{2+}.

Greater complexity is observed for $Au(SO_3F)_2$ in particular in the SO_3F-stretching region. Interestingly, the previously reported vibrational spectra of $Au(SO_3F)_3$ [5a] provide a better basis for a spectral comparison, than do the spectra of $Ag(SO_3F)_2$ [19] and $Cu(SO_3F)_2$ [20][21]. Similarity in band shapes and band positions is evident from the tracing of the IR spectra shown in Fig. 1 and the band listings and tentative assignments in Table 1. This similarity involves bands in the SO_3F-stretching region, and the presence of bidentate bridging and monodentate fluorosulfate groups is implied for both $Au(SO_3F)_2$ and $Au(SO_3F)_3$.

The molecular structure of the gold(III) compound reveals a dimeric molecule, with nearly square planar AuO_4-groups and symmetrically bridging bidentate, as well as terminal, fluorosulfate groups [6].

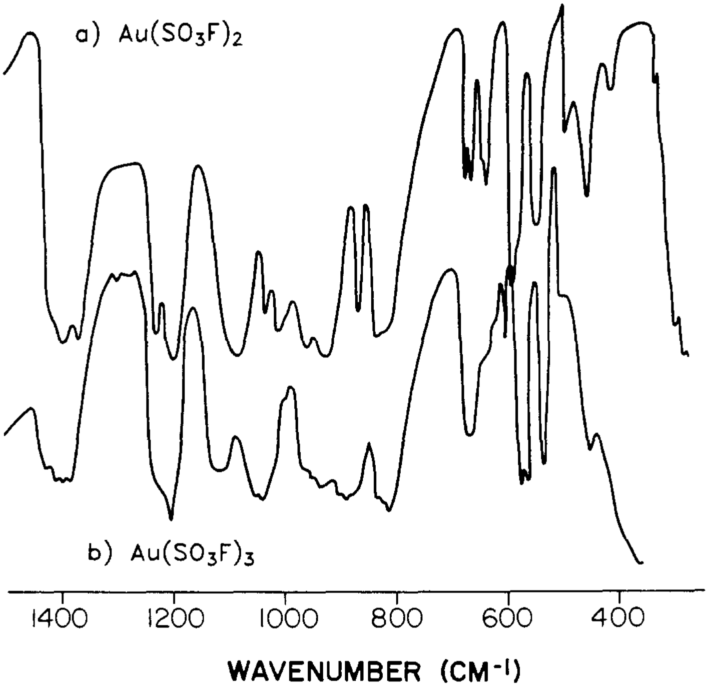

Fig. 1. The infrared spectra of $Au(SO_3F)_2$ and $Au(SO_3F)_3$ between 1500 and 400 cm^{-1}.

A similar coordination mode of the fluorosulfate groups in gold(II)-fluorosulfate is best interpreted in terms of an oligomeric mixed valency compound with linearly coordinated Au(I)(d^{10}), and square planar Au(III)(d^8) metal centers as found in $Au(SO_3F)_3$ [6]. The molecular structure of Au_4Cl_8 [3] may be viewed as a related precedent and the observed diamagnetism is now easily accounted for. A different degree of oligomerisation, or even a chain structure, is of course possible for the fluorosulfate.

TABLE 1

The Vibrational Spectra of $Au(SO_3F)_2$ and the IR Spectrum $Au(SO_3F)_3$[a]

$Au(SO_3F)_2$ Raman	$Au(SO_3F)_2$ IR	$Au(SO_3F)_3$ IR	Approximate	$Au(SO_3F)_2$ Raman	$Au(SO_3F)_2$ IR	$Au(SO_3F)_3$ IR	Approximate
$\Delta\bar{\nu}$[cm^{-1}] Int.	$\bar{\nu}$[cm^{-1}] Int.	$\bar{\nu}$[cm^{-1}]	Description	$\Delta\bar{\nu}$[cm^{-1}] Int.	$\bar{\nu}$[cm^{-1}] Int.	$\bar{\nu}$[cm^{-1}]	Description
1423 s	1418 s, sh	1442	νSO_3as		680 ms	682	$\nu Au^{III}O_4$
1409 m	1400 vs	1425	bi and t	668 w	671	670	+def as
1393 w	1369 s						
1375 w				642 s	648 m, sh		
1226 s	1232 s	1240	νSO_3sym				$\nu Au^{I}O_2$
			t		640 m		+def as
1199 w,sh	1200 vs	1220	νSO_3sym			610	
1114 w			bi	600 ms	595 s	590	δSO_3 as
	1085 s, b	1135		577 w	585 ms, sh	582	bi + t
1044 w	1065 m, sh	1055	νSO_3sym				
1025 w	1035 ms		bi	541 m	548 ms	552	δSO_3sym
1010 w	1012 ms						
993 w				456 m	462 m	460	$\nu Au^{III}O_4$·def
955 w	962 ms	960	νSO-Au	450 m			
	931 s	920	t	415 w	418 w		ρSO_3F
				307 w			bi + t
867 vw	870 ms	895		274 vs			
845 w	836 s		νSF	258 m			various def.
823 w	822 s, sh	820	bi and t	194 m			and torsion
	812 s, sh			184 m			modes
				136 w			

[a] Ref. 5a.

Abbreviations

$\Delta\bar{\nu}$ = Raman shift in cm^{-1}, $\bar{\nu}$ = wavenumber in cm^{-1}, Int. = estimated intensity, s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, bi = bidentate bridging, t = terminal monodentate, def = deformation mode, ν = stretch, δ = bend, ρ = rock, sym = symmetrical, as = antisymmetrical.

The small differences in band positions and intensities apparent in Table 1 are now readily explained: Bands attributed to bridging SO_3F-groups are more prominent in the spectrum of $Au(SO_3F)_2$ and greater band proliferation is attributed to the presence of slightly different acceptor sites, with Au(I) and Au(III) possibly resulting in unsymmetrical fluorosulfate bridges giving rise to lower overall molecular symmetry for the mixed valency compound. Finally, a set of two closely spaced bands at ~645 cm^{-1} found only in the spectrum of $Au(SO_3F)_2$ is attributed to AuO_2-skeletal vibrations. When excitation with either Ar^+ (514.5 nm) or Kr^+ (647.1 nm) is used, only a poor Raman spectrum of the gold(II) fluorosulfate is obtained. On the other hand with a Fourier Raman spectrometer a reasonably complete spectrum is obtained and the measured Raman shifts are listed in Table 1. There is good correspondence between IR and Raman band positions, an indication of the low symmetry of the material.

While a Au(I) Au(III) compound is suggested by the vibrational spectra, an alternative structural proposal of Au(III) centers only linked by a Au-Au bond cannot be ruled out, but is deemed less likely.

With solid gold(II) fluorosulfate clearly diamagnetic, it is surprising that the suspension of the solid in fluorosulfuric acid, obtained after the completed reduction at 25°C, gives rise to an intense, anisotropic ESR spectrum. The signal persists unchanged in the dark red-brown solution, when the solid is removed by filtration. The spectrum is shown in Fig. 2, curve (b).

ESR active gold(II) complexes, in particular those with dithiolate ligands, have been reported previously [1][24], but all reported spectra differ substantially from the one obtained by us. Previously reported g_{iso} values are well below 2.10 [1][24], while a g_{iso} value of 2.318 is found here. Subsequently in a careful analysis of a previously observed spectrum, the authors have concluded that the unpaired electron in those complexes resides

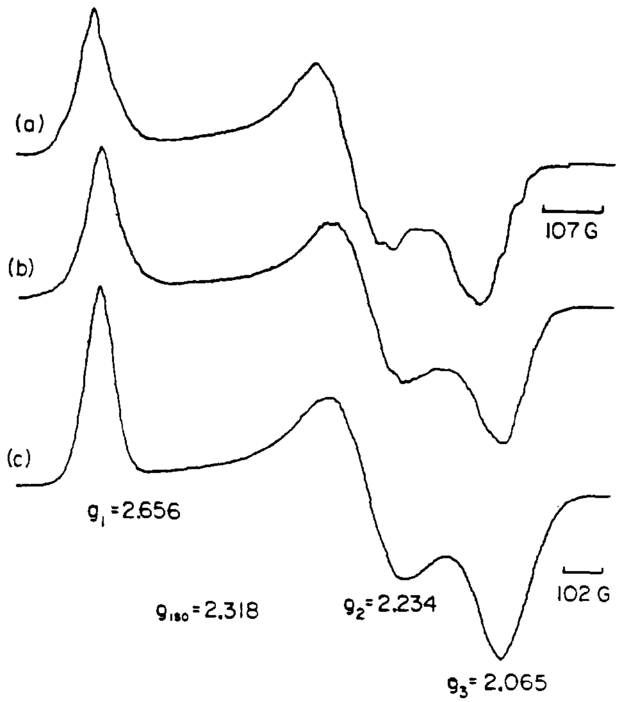

Fig. 2. The ESR spectrum of Au^{2+} (solv.)(a)(b) and the simulated spectrum (c).

primarily on the ligand [25]. As seen in Fig.2, (curve(b))the spectrum displays a very large g-anisotropy together with a line shape that is inhomogeneously broadened. The large anisotropy of the g-tensor (g_1 = 2.656, g_2 = 2.234 and g_3 = 2.065) suggest a radical based on a transition metal ion with a large spin orbit coupling, i.e. gold [26], in this system. The form of the tensor suggests a site symmetry of C_{2v} or less for the gold. The presence of inhomogeneous broadening is to be inferred by the relative intensities of the three g-manifolds. Typically, in the absence of inhomogenous broadening, the manifold due to the central g-value is of derivative form and of greater apparent intensity than the other two. In the present case the central resonance has diminished intensity due to inhomogeneous broadening. Careful inspection (using a second derivative) of the highfield resonance reveals the presence of a quintet suggesting the presence of four F-atoms in the coordination sphere of the Au(II). Far better resolved HFS is observed at a slightly different concentration and the quintet is now recognizable without the aid of a second derivative (curve (a)). Therefore simulations were performed using unresolved hyperfine from four F-atoms.

The simulation, using a fluorine hyperfine coupling tensor of $A_1 = 65$ MHz, $A_2 = 112$ and $A_3 = 79$ MHz for four ^{19}F nuclei and linewidths $L_1 = 60$ G, $L_2 = 98$ G and $L_3 = 74$ G for Lorentzian lines, is displayed as the curve (c) in Fig. 2. Comparison of the three curves in Fig. 2 shows a close correspondence providing evidence for the interpretation of a Au^{2+} surrounded by four fluorosulfate anions.

The question arises why is the ^{197}Au hyperfine not observed. The principal reason for this is the small nuclear moment for Au (about 50 times less than that of ^{19}F). Consequently, with the electron in any orbital which provides comparable spin density on gold and fluorine, the observation of ^{19}F hyperfine is more likely. The results of the ESR study indicate that the Au(II) is surrounded by four fluorosulfate groups in a distorted arrangement.

We have subsequently, under different conditions generated a more symmetrically coordinated Au^{2+} species in HSO_3F solution when $Au(SO_3F)_3$ is present in excess, as well as in the solid state [27] and studied this ion by ESR. The importance of the spectrum reported here is twofold:

(i) it represents the first time a true Au^{2+} species was detected by ESR, and

ii) it establishes a connection between diamagnetic gold(II), assumed to be a mixed valency Au(I)-Au(III) fluorosulfate, and paramagnetic $Au^{2+}_{(solv.)}$ with both produced in the same reaction.

A precedent for such an equilibrium is found in the chemistry of silver(II) [28]. When solid argentic oxide, AgO, formulated as Ag(I)Ag(III)O_2, is dissolved in strong mineral acids, paramagnetic $Ag^{2+}{}_{(solv.)}$ is generated according to:

$$AgO + 2H^+ \longrightarrow Ag^{2+} + H_2O \qquad (4)$$

In our case, the presence of $Au^{2+}{}_{(solv.)}$ in solution explains why $Au(SO_3F)_2$ is obtained in approximately 80% yield.

CONCLUSIONS

The study described here emphasizes the usefulness of fluorosulfuric acid in the straightforward synthesis of a rare example of a mixed valency gold(I)-gold(III)compound and, by virtue of its ionizing ability, allowing stabilisation of the rather unusual Au^{2+} cation in the same reaction.

ACKNOWLEDGEMENT

Financial support by the Natural Science and Engineering Research Council of Canada (to F.G.H. and F.A.), Deutsche Forschungsgemeinschaft (to H.W.) and to NATO, Collaborative Research Grants Programme (to F.A. and H.W.) is gratefully acknowledged. Dr. Sawatzki, of Bruker Analytische Messtechnik, Karlsruhe, F.R.G. is thanked for recording the Raman spectrum.

REFERENCES

1 a) R. J. Puddephatt, 'The Chemistry of Gold', Elsevier, Amsterdam 1978, and references therein.

b) R. J. Puddephatt, in G. Wilkinson (ed), 'Comprehensive Coordination Chemistry', Pergamon Press, Oxford 1987, Vol. 7, 861 and references therein.

2 B. J. Müller, Angew. Chem. Int. Ed. Engl. 26. (1987) 1081.

3 a) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, S. Merlino and G. Perego, J. Chem. Soc. Chem. Commun., (1977) 131.

b) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, J. Chem. Soc. Dalton Trans., (1982) 2257.

4 W. M. Johnson, R. Dev and G. H. Cady, Inorg. Chem. 11. (1972) 2260.

5 a) K. C. Lee and F. Aubke, Inorg. Chem. 18. (1979) 389.

b) K. C. Lee and F. Aubke, Inorg. Chem. 19. (1980) 119.

6 H. Willner, S. J. Rettig, J. Trotter and F. Aubke, submitted for publication.

7 H. Willner and F. Aubke, Inorg. Chem. 29. (1990) 2195.

8 a) A. W. Jache, Adv. Inorg. Chem. and Radiochem. 16. (1974) 177.

b) R. J. Gillespie, Acc. Chem. Res. 1. (1968) 202.

c) R. C. Thompson in G. Nickless (ed.), 'Inorganic Sulfur Chemistry', Elsevier, Amsterdam 1968, 587.

9 G. H. Cady and J. M. Shreeve, Inorg. Synth. 7. (1963) 124.

10 J. Barr, R. J. Gillespie and R. C. Thompson, Inorg. Chem. 3. (1964) 1149.

11 F. G. Herring and P. S. Phillips, J. Magn. Reson. 62. (1985) 19.

12 J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, Can. J. Chem. 62, (1982) 891.

13 W. Gombler and H. Willner, J. Phys. E. Sci. Instrum. 20. (1967) 1286

14 D. R. Shriver, 'The Manipulation of Air-Sensitive Compounds', McGraw-Hill, New York, 1969.

15 J. N. Brazier and A. A. Woolf, J. Chem. Soc. A, (1967) 99.

16 T. C. Waddington, Trans. Farad. Soc. 55. (1959) 1531.

17 H. Willner and F. Aubke, to be published.

18 K. C. Lee and F. Aubke, Can. J. Chem. 55. (1977) 2473.

19 P. C. Leung and F. Aubke, Inorg. Chem. 17. (1978) 1765.

20 J. Goubeau and J. B. Milne, Can. J. Chem. 45. (1967) 2321.

21 A. L. Arduini, M. Garnett, R. C. Thompson and T. C. T. Wong, Can. J. Chem. 53. (1975) 3812.

22 M. S. R. Cader, R. C. Thompson and F. Aubke, Chem. Phys. Lett. 164. (1989) 438.

23 C. S. Alleyne, K. O'Sullivan Mailer and R. C. Thompson, Can. J. Chem. 52. (1974) 336.

24 Landolt-Börnstein. Numerical data and functional relationships in science and technology, Vol. 2. Supplement II. Magnetic properties of coordination and organometallic transition metal compounds. Springer Verlag, Berlin, 1966 and 1976.

25 R. L Schlupp and A. H. Maki, Inorg. Chem., 13 (1974) 44.

26 B. N. Figgis, 'Introduction to Ligand Fields', Interscience , New York 1966.

27 F. G. Herring, G. Hwang, K. C. Lee, F. Mistry, P. S. Phillips, H. Willner and F. Aubke, submitted for publication to J. Am. Chem. Soc..

28 J. A. McMillan, Chem. Rev. 62. (1962) 65 and references therein.