

Eight-Coordination. II.¹ Synthesis and Spectroscopic and Structural Properties of Tetrakis(dithiocarboxylato)molybdenum(IV)

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Several dithiocarboxylato complexes of Mo(IV) have been prepared and characterized. They are diamagnetic, eight-coordinate species with a common dodecahedral symmetry in the MoS₈ chromophore. Electronic spectra of the title complexes reveal a higher degree of covalency in the metal-ligand bond than is found in any other eight-coordinate species of Mo(IV). The influence of π -bonding interactions on the stereochemical behavior of eight-coordinate dithiocarboxylato complexes is discussed.

Introduction

The chemistry of molybdenum dithiocarbamate and xanthate complexes has been investigated in considerable detail.² In contrast no information is available in the literature on dithioaromatic or dithioaliphatic acid derivatives of molybdenum. As part of a continuing study of both eight-coordination chemistry of transition metal ions¹ and coordination chemistry of dithiocarboxylates,³ we have obtained a new series of Mo(IV) complexes of type Mo(RCSS)₄, for which molecular and electronic structural data are reported. These are of interest since they can be compared with those obtained for the analogous V(IV) complexes¹ (3d¹ systems) and with those for eight-coordinate species of Mo(IV) involving the CN⁻ ligand,^{4,5} which appear to be the most investigated eight-coordinate complexes of Mo(IV).

Experimental Section

Ligands. Dithio acids and sodium salts were prepared following known procedures: C₆H₂CSSH (dtbH),⁶ *p*-CH₃OC₆H₄CSSH (mdtbH),⁷ C₆H₅CH₂CSSH (dtpaH).⁸

M₃MoCl₆. Molybdenum(III)-hexachloro complexes with M = (*n*-C₄H₉)₄N⁺ (TBA) and (C₂H₅)₄N⁺ (TEA) were prepared by electrolytic reduction from MoO₃ analogously to ref 9 and 10.

Mo(dtbt)₄. (TBA)₃MoCl₆ (0.5 g, 5 × 10⁻⁴ mol) was added to 70 ml of EtOH. The mixture was refluxed for 10 min and the resulting reddish solution was filtered. To this, an orange-red solution of dtbH (0.79 g, 5 × 10⁻³ mol) in CH₂Cl₂ (70 ml) was added, with stirring. In a few minutes the color of the reaction mixture turned to violet and after ~1 hr dark violet crystals began to form. Complete precipitation was achieved in ~12 hr, at room temperature. The crystals were filtered, washed with petroleum ether, and dried under vacuum. They were not recrystallized; yield ~30%, based on original molybdenum. By using the same mole ratio as above, higher yields could be obtained by increasing the concentration of the starting solutions. This has the disadvantage that smaller crystals are formed than in the case of dilute solutions. *Anal.* Calcd for C₂₈H₂₀S₈Mo: C, 47.44; H, 2.85; S, 36.18; Mo, 13.53; mol wt 709. Found: C, 47.56; H, 2.97; S, 36.04; Mo, 12.95; mol wt 721 (in methylene chloride); mp 227–228°.

(1) Part I: O. Piovesana and G. Cappuccilli, *Inorg. Chem.*, **11**, 1543 (1972).

(2) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 311 (1970), and references therein.

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Mo(dtpa)₄. A solution of dtpaNa (5 g, 5.3 × 10⁻² mol) in H₂O (50 ml) was acidified with HCl and extracted with CH₂Cl₂ (100 ml). A mixture of (TEA)₃MoCl₆ (1.8 g, 2.6 × 10⁻³ mol) in 80 ml of EtOH was refluxed for 10 min. The resulting red solution was filtered and added, with stirring, to the red CH₂Cl₂ solution of dtpaH. The reaction mixture was refluxed for 1 hr. The color turned from red to dark green but no precipitate formed. The volume of the solution was then reduced to ~100 ml by evaporation under vacuum and a dark gummy mass formed which was washed with petroleum ether and dried under vacuum. Dark crystals, in ~20% yield, were obtained upon crystallization from absolute EtOH; mp ~61° dec. *Anal.* Calcd for C₃₂H₂₈S₈Mo: C, 50.24; H, 3.69; S, 33.53; Mo, 12.54; mol wt 765. Found: C, 49.71; H, 3.58; S, 33.36; Mo, 12.21; mol wt 730 (in acetone).

Mo(mdtb)₄. In a manner similar to that described above for the dithiobenzoate derivative, (TEA)₃MoCl₆ (1.8 g, 2.6 × 10⁻³ mol) was dissolved in EtOH (75 ml), the solution was filtered, and to this mdtbH (3.8 g, 2 × 10⁻² mol) in CH₂Cl₂ (75 ml) was added. The resulting solution was refluxed for 2 hr and then evaporated under vacuum until a dark gummy mass separated. This was crystallized twice from CS₂, and well-formed black-violet crystals were obtained (0.4 g, 19% yield). *Anal.* Calcd for C₃₂H₂₈O₄S₈Mo: C, 46.36; H, 3.40; S, 30.94; Mo, 11.57; mol wt 829. Found: C, 45.96; H, 3.30; S, 31.92; Mo, 12.12; mol wt 728 (in acetone); mp 224–225°.

Measurements. Chemical Analyses. These were performed by Alfred Bernhardt Mikroanalytisches Laboratorium and by Laboratorio di Microanalisi, Padua, Italy.

Molecular Weights. Molecular weight measurements were made with a Mechrolab Model 301-A vapor pressure osmometer. Methylene chloride and acetone were used as solvents.

Infrared Spectra. These were measured on Nujol and Fluorolube mulls on Perkin-Elmer 521 and Beckman IR 10 spectrophotometers, in the region 5000–350 cm⁻¹.

Visible-Uv Spectra. Both solution and solid-state spectra were recorded on a Beckman DK 1A spectrophotometer.

Magnetic Moments. Magnetic susceptibilities were measured at room temperature on solid polycrystalline samples, by the Gouy method. Pascal's constants were used to correct the measurements for diamagnetism of the cation and the ligands. All the complexes exhibited some degree of paramagnetism up to 0.5–0.6 BM which was field dependent, was nonreproducible, and was of decreasing intensity on repeated recrystallization. Ferromagnetic impurities are probably responsible for such behavior.

Nmr Spectra. ¹H nmr spectra were recorded by a JEOL C60 HL spectrometer. Reported chemical shifts were measured working in internal lock (TMS or DSS was used for locking signals).

Results

Several molybdenum(IV) dithiocarboxylates have been synthesized by reaction between hexachloromolybdates(III) of suitable organic cations and the appropriate dithiocarboxylic acids in mixed solvent solutions (usually ethanol-methylene chloride).

Analytical data indicate a common Mo(RCSS)₄ stoichiometry. The Mo(RCSS)₄ species have similar properties. They are unaffected by atmospheric oxygen and can be kept unaltered for a long time. They are practically insoluble in polar solvents such as water or ethanol and are slightly solu-

Table I. Infrared Frequencies (cm^{-1}) and Assignments of the Characteristic Absorptions of the $\text{Mo}(\text{RCSS})_4$ Complexes

	$\bar{\nu}$ (phenyl-C)	$\bar{\nu}_{\text{as}}$ (CSS)	$\bar{\nu}_{\text{s}}$ (CSS)	δ (CSS)	$\bar{\nu}_{\text{as}}$ (MSS)	$\bar{\nu}_{\text{s}}$ (MSS)
$\text{Mo}(\text{dtb})_4$	1265 s	1018 s	945 m	665 m	370 w	331 m
$\text{Mo}(\text{mdtb})_4$	1270 s	1035 s	952 m	675 w	380 sh?	329 s 321 s
$\text{Mo}(\text{dtpa})_4$	1253 ms	1028 s	951 m	658 m, 649 w	370 vw?	320 w, br

ble in nonpolar or weakly polar organic solvents such as acetone, benzene, chloroform, methylene chloride, or carbon disulfide (order of magnitude $\sim 5 \times 10^{-3} M$, at room temperature).

Solutions of the complexes in the above solvents are quite stable, as shown by the fact that their electronic spectra remain unchanged for several days.

Molecular weight data (osmometric) are rather inaccurate due to the low solubilities; however, they clearly suggest monomeric species for all the complexes. The X-ray structure determination of $\text{Mo}(\text{dtb})_4$ confirms this.

The molybdenum(IV) dithiocarboxylates are diamagnetic. The small paramagnetism (0.5–0.6 BM) is ascribed to the presence of ferromagnetic impurities, as in the case of dithiocarboxylates of other metals^{1,3,11} and, in part, to temperature-independent paramagnetism. The diamagnetism of the complexes is confirmed by proton nmr measurements in CDCl_3 (*vide infra*) which show "normal" phenyl resonances, without paramagnetic shifts.

Spin-paired octacoordinate d^2 species are generally inert.¹² In order to test qualitatively the labile or inert character of our complexes, $\text{Mo}(\text{dtb})_4$ was dissolved in a CH_2Cl_2 solution containing a 40:1 excess of dtpaH . The solution was refluxed for 2 days under nitrogen. No variation of the electronic absorptions of $\text{Mo}(\text{dtb})_4$ was observed and upon concentration of the solution the dithiobenzoato complex was recovered unaltered.

Crystals of $\text{Mo}(\text{dtb})_4$ were suitable for X-ray analysis and this was performed by Bonamico, *et al.*, in a parallel investigation.¹³ Crystals are tetragonal, space group $I4_1/a$. There are four $\text{Mo}(\text{dtb})_4$ molecules in the unit cell, each molybdenum atom being in special position on the $\bar{4}$ axis. The coordination sphere of the metal atom is dodecahedral, the eight sulfur atoms being at the vertices of two right-angle, interlocking trapezoids.

The vibrational spectra of the $\text{Mo}(\text{IV})$ complexes in the KBr region are typical of completely chelated dithiocarboxylato complexes and are interpreted following previous lines of assignment.^{1,14–16} Selected frequencies are reported in Table I.

The vibrations of the organic skeleton in the corresponding $\text{Mo}(\text{IV})$ and $\text{V}(\text{IV})^1$ complexes show no significant differences.

¹H nmr measurements of the $\text{Mo}(\text{RCSS})_4$ species gave limited information due to the low solubility of the complexes. The chemical shifts are reported in Table II.

In the spectrum of $\text{Mo}(\text{mdtb})_4$ the para CH_3O group gives a sharp line and the aromatic protons give a quartet. Formally the aromatic protons in the chelated ligand form an

Table II. Chemical Shifts (ppm from TMS) of the $\text{Mo}(\text{RCSS})_4$ Complexes and of the Parent Ligands

Compd	Solvent	Phenyl		CH_3 , $-\text{CH}_2-$
		Ortho	Meta, para	
$\text{Mo}(\text{mdtb})_4$	CDCl_3	7.95, 7.78	6.87, 6.73	3.82
mdtbH	CDCl_3	8.06 ^b	6.93 ^b	3.88
$\text{Mo}(\text{dtb})_4$	CDCl_3	7.85 ^b	7.30 ^b	
dtbNa	D_2O	7.84 ^{a,b}	7.31 ^{a,b}	
$\text{Mo}(\text{dtpa})_4$	CDCl_3		7.25 ^b	3.95

^a Ppm from DSS. ^b Centers of multiplets.

AA'BB' system, but due to the large chemical shifts between ortho and meta protons, the spectrum approximates a simple four-line AB pattern. All the protons in the complex are more shielded (higher resonance frequencies) than in the free ligand mdtbH. In the latter, restricted rotation about the C–CS₂H bond is suggested by the inequivalence of the protons ortho to the CSSH group (resonances at 7.99, 8.09, 8.12, and 8.24 ppm), and, less clearly, the same inference might be made from the meta protons.

The spectrum of dtbNa shows complicated patterns; however resonances at 7.7–8.0 and 7.1–7.5 ppm may be attributed to the ortho and to the para, meta protons, respectively. $\text{Mo}(\text{dtb})_4$ shows similar absorptions but comparison of the chemical shifts is impossible because of the different solvents. $\text{Mo}(\text{dtpa})_4$ shows magnetic equivalence of the CH_2 groups.

The electronic absorption spectra of the molybdenum(IV) dithiocarboxylates are reported in Table III and Figure 1. Solution and solid-state spectra, although not identical, exhibit small differences. A high intensity characterizes all the absorptions of the three complexes. The introduction of the electron-releasing para MeO substituent appears to have little influence on the spectroscopically accessible energy levels of $\text{Mo}(\text{dtb})_4$. The aryl-aliphatic-substituted complex shows less intense bands than the aryl-substituted species, as was the case for the corresponding $\text{V}(\text{IV})$ complexes,¹ and at slightly different energies. Particularly the very intense band at ~ 11 kK in the spectra of the dtb and mdtb complexes seems to be absent in the spectrum of $\text{Mo}(\text{dtpa})_4$.

Discussion

The tetrakis(dithiocarboxylato)molybdenum(IV) complexes are monomeric, stable eight-coordinate species.

Their synthesis from $\text{Mo}(\text{III})$ starting materials indicates stabilization of the metal +4 oxidation state by the ligands, as is the case^{1,4} for $\text{Mo}(\text{CN})_8^{4-}$ and $\text{V}(\text{RCSS})_4$. Dodecahedral coordination geometry for $\text{Mo}(\text{dtb})_4$ was established by X-ray structure determination,¹³ and it is reasonable to assume the same basic geometry for the complexes with the dtpa and mdtb ligands, due to the strong similarities in the chemical and physical properties, particularly the electronic spectra, of the three compounds.

The mentioned coordination geometry is presumably retained in solutions of weakly polar solvents, as differences between solid-state and solution electronic spectra are small.

Magnetic Properties. The molybdenum(IV) dithiocarboxylates are spin-paired d^2 species, which is in agreement with the observed dodecahedral, D_{2d} symmetry. This per-

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Table III. Electronic Spectra of the L⁻ Ligands and Their Mo(IV) Complexes^{a, b}

Compd	Medium						
Mo(dtb) ₄	CH ₂ Cl ₂	11.6 (4.15)	13 sh	17.6 (3.83)	20.8 (3.68), 21.5 sh	30.8 (4.75), 33.9 (4.84)	
	Reflectance	11.4		16.8	20.0	<i>d</i>	
dtbNa ^e	H ₂ O				20.8 (2.15)	28.2 (3.70), 34.1 (3.63)	
dtbH ^e	(C ₂ H ₅) ₂ O				19.0 (1.83)	30.0 (3.66), 33.7 (3.98)	
Mo(mdtb) ₄	CHCl ₃	11.3 (4.19)	12.1 sh, 12.9 sh	17.9 (3.84)	21.5 sh (3.69), 23.0 sh (3.73)	30.8 (5.03), 35.7 (5.13)	
	Nujol	11.1	12.0 sh	16.8	21.1, 22.8	<i>d</i>	
mdtbH	CHCl ₃				19.9 (2.13)	28.7 (4.10), 35.1 (3.74)	
Mo(dtpa) ₄	(CH ₃) ₂ CO		13.5 (3.28)	17.1 (3.28)	22.3 (3.38), 25.0 sh		
	CHCl ₃		13.6 (3.44)	17.4 (3.45)	22.2 (3.53), 25.0 sh (3.36)	29.4 sh, 35.8 sh	
	Reflectance		13.2	~16 ^c	21.8 sh	<i>d</i>	
dtpaNa ^e	H ₂ O				20.8 (1.65)	29.4 (3.90)	
dtpaH ^e	(C ₂ H ₅) ₂ O				20.8 (1.36)	34.1 (3.74)	

^a Absorption maxima in kK. ^b sh = shoulder; log ε in parentheses. ^c Very broad band. ^d Not measured beyond this frequency. ^e Data from ref 1, 3.

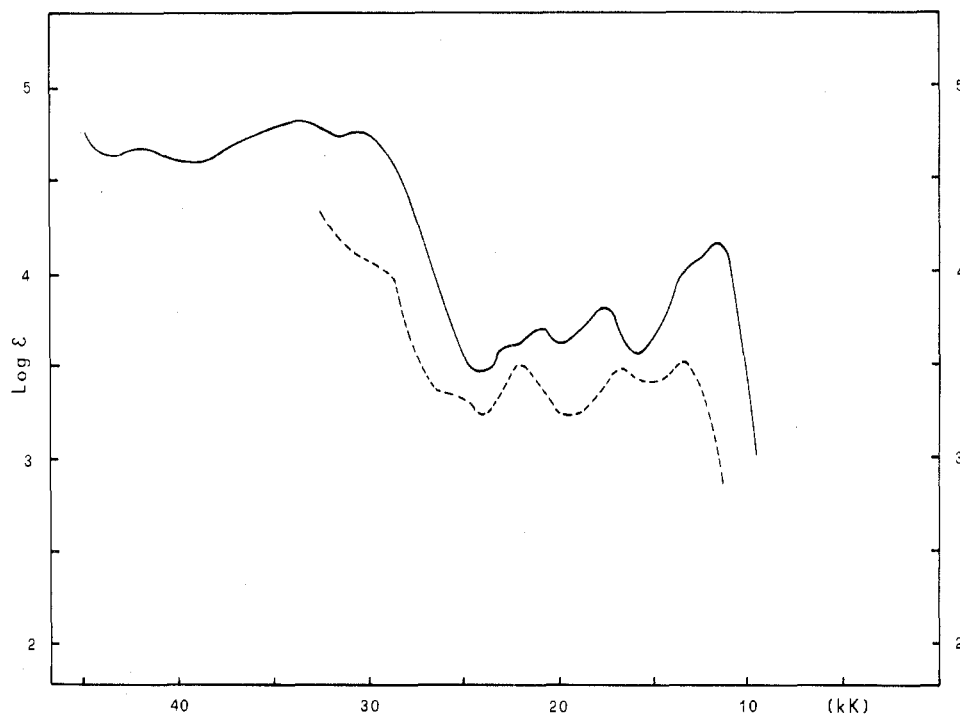


Figure 1. Absorption spectra: —, Mo(dtb)₄ in CH₂Cl₂; ---, Mo(dtpa)₄ in CHCl₃.

mits that the $d_{x^2-y^2}$ (B_1) metal orbital be involved in π but not in σ bonding to the ligands and therefore the two electrons are expected to occupy a low-lying, d-like energy level, orthogonal to the σ -bonding matrix and capable of π bonding.

Spin-paired Mo(IV) would be anticipated also in a hypothetical antiprismatic geometry since in D_{4d} symmetry the d_{z^2} (A_1) metal orbital, although having the correct symmetry, contributes practically nothing to the σ -bonding matrix. In this respect, a recent report¹⁷ of the apparently eight-coordinate tetrakis(tetramethylenedithiocarbamate)molybdenum(IV) having a high-spin behavior ($\mu = 2.11$ BM) is rather surprising. This compound is different from ours also in having low intensity d-d transitions at 18.9, 21.3, and 22.2 kK. The only other sulfur-donor, potentially eight-coordinate complex of Mo(IV) known to the authors is Mo(S₂CNMe₂)₄, for which only chemical analyses have been reported.¹⁸ Structural characterization of these complexes would be helpful to explain the magnetic and spectroscopic differences between molybdenum(IV) dithiocarboxylates and dithiocarbamates.

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Electronic Spectra. Internal ligand $\pi \rightarrow \pi^*$ transitions in metal dithiocarboxylato complexes are usually observed above ~ 28 kK.^{1,3,19} Absorptions apparently of this type are shown by the spectra of the Mo(RCSS)₄ species at ~ 30 and ~ 34 kK. In addition, up to six bands are observed for the latter complexes, between ~ 11 and ~ 25 kK, and, in ligand field language, most of them should be assigned to charge-transfer transitions by virtue of the high intensities ($\epsilon \sim 2000$ –14,000). A d-d origin cannot obviously be discounted for some shoulders (e.g., at ~ 13 and ~ 22 –23 kK for the aromatic complexes and at 25 kK for Mo(dtpa)₄) which could be intensified mainly by borrowing the intensity from the nearest strong bands. Single-crystal polarized spectra of Mo(dtb)₄ are in order to clarify this point. Be $M \rightarrow L$ or $L \rightarrow M$ the character of the charge-transfer transitions, it has to be admitted that in order for all the ligand field transitions to be obscured or merged, some of the π^* orbitals of the ligand system are almost degenerate with the filled π -bonding ($d_{x^2-y^2}$) or the mainly σ -antibonding d orbitals of the central metal ion. The general picture is one of an efficient mixing of metal and ligand orbitals which does not justify a simple localization of valence orbitals as

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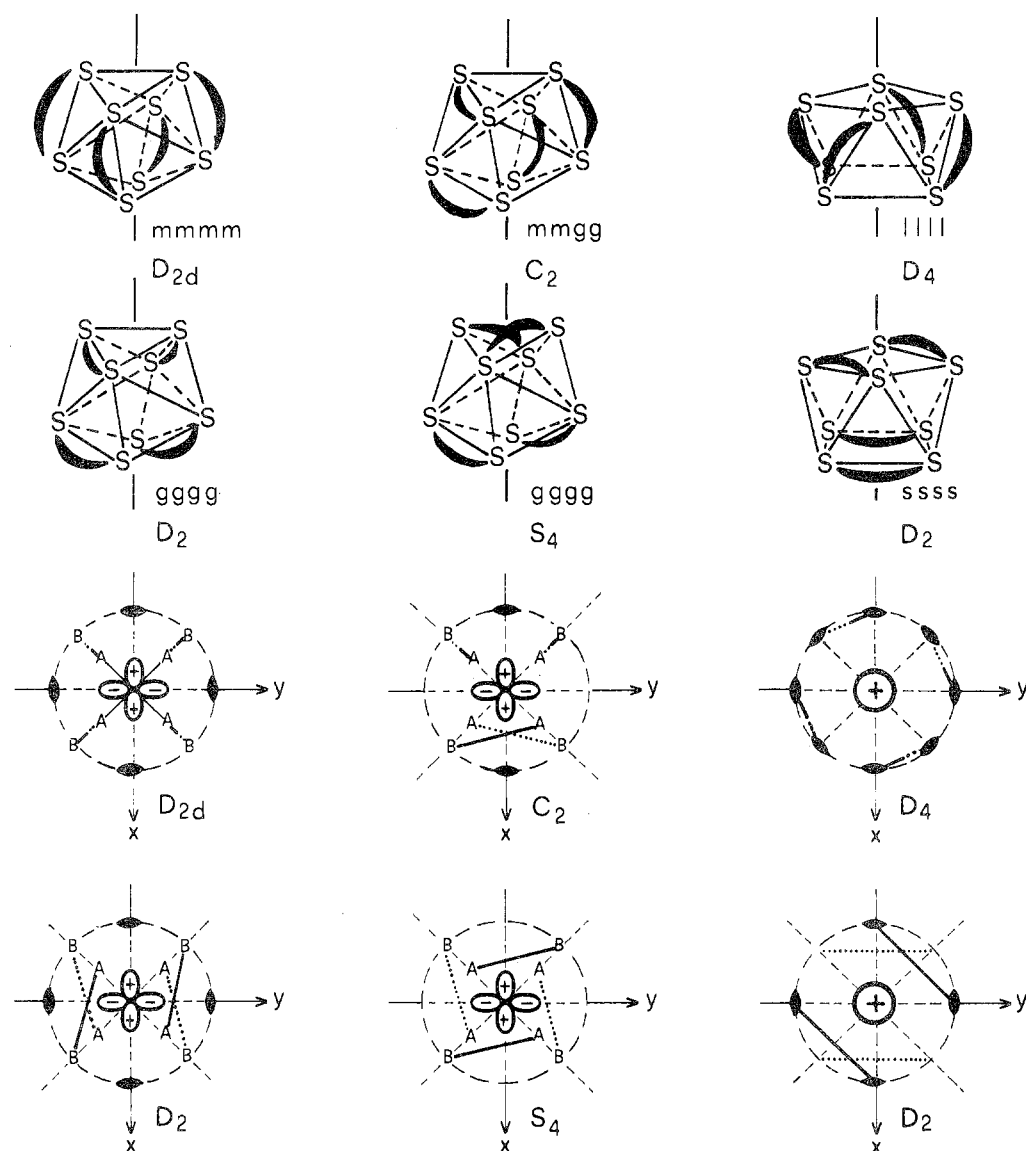


Figure 2. D_{2d} , D_2 , and S_4 dodecahedral and D_4 and D_2 square-antiprismatic isomers for $M(RCSS)_4$. The dodecahedral C_2 isomer, of importance [L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, *Acta Crystallogr., Sect. B*, **28**, 1298 (1972)] for $V(\text{dithioacetato})_4$, is also shown. Polyhedral edges are labeled according to J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963). In the stereographic projections the σ nonbonding metal orbitals are depicted together with the projections of the ligand bites [(—) above and (· · · ·) below the equatorial plane], to which the donor atoms π orbitals are perpendicular.

ligand field, charge transfer, or internal ligand. This behavior is not observed in the other eight-coordinate Mo(IV) complexes which have been studied spectroscopically, for example, $\text{K}_4\text{Mo(CN)}_8 \cdot 2\text{H}_2\text{O}$,²⁰ $(\text{RNC})_4\text{Mo(CN)}_4$,⁵ and $\text{Mo}(\text{S}_2\text{CN}(\text{CH}_2)_4)_4$.¹⁷ A suitable MO treatment is clearly needed for an appropriate description of the electronic structure of the molybdenum(IV) dithiocarboxylates. Until the latter becomes available, it is useful to see whether the stereochemical behavior of the eight-coordinate dithiocarboxylates might be related to the electronic structure of the ligand system and how the ligand's molecular orbitals interact with the metal valence functions upon complexation. Our attention will be focused on π bonding.

Stereochemical Behavior and π Bonding. Figure 2 shows the three dodecahedral and the two square-antiprismatic isomers which are possible for a metal tetrakis chelate in which the four chemically identical ligands span equivalent polyhedral edges.²¹ A general discussion of these stereo-

isomers can be found in ref 4 and 21–23. Structural information about $\text{Mo}(\text{dtb})_4$ and $\text{V}(\text{dtb})_4$ is summarized in Table IV. The two complexes adopt the dodecahedral D_{2d} configuration, and the values of d_i together with the angles between the best least-square planes defining the two intersecting trapezoids²⁴ indicate that deviations from the idealized geometry are very small. It is noteworthy that ligand–ligand repulsive energy minimization would favor a different stereochemistry.

Calculations were carried out by Blight and Kepert²⁵ and show that the potential energy minima (corresponding to the various dodecahedral and antiprismatic stereoisomers of metal tetrakis chelates in which the bidentate ligands span equivalent polyhedron edges) are dependent upon the normalized ligand bite "b." For a "bite" 1.10–1.11 Å, as ob-

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(23) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

(24) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

(25) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).

served in the dithiocarboxylato complexes, a single, very broad minimum appears on the potential energy surface which encompasses both the D_{2d} dodecahedron and the distorted D_2 square antiprism, corresponding to dihedral angles of about 5 and 18°, respectively. The expected intermediate structure is not verified by the dtb complexes. There is agreement between the calculated angular parameters $\vartheta_A = 39^\circ$, $\vartheta_B = 75^\circ$, and those reported in Table IV, but it is doubtful whether this agreement is really significant since, as discussed by Lippard and Russ,²⁴ ϑ_A and ϑ_B provide a poor criterion to identify a particular eight-coordinate complex with either idealized polyhedron.

Turning to the possible stereochemical role of π bonding in the dithiobenzoato complexes, a first observation is that all the



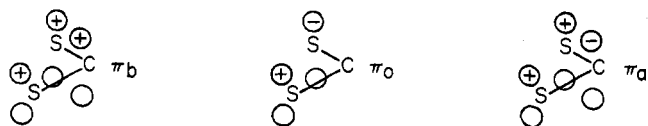
chelated rings are planar and the MSC angles deviate by not more than 2° from 90°. This indicates that, in a valence-bond formalism, p orbitals are mainly engaged by sulfur in the S-M and S-C σ bonds. Consequently the donor atom π orbitals are directed perpendicularly to the chelated ring (π_v). In the zero-overlap approximation, the carbon $2p\pi$ AO and two sulfur $3p\pi$ AO's of the CS_2^- group combine into three MO's: π_b , π_o , π_a .^{26,27} In the ground state, each of the two lower π_v orbitals, π_o and π_b , is occupied by two electrons, and the highest orbital, π_a , is vacant.

We assume, as a first approximation, that only metal orbitals not engaged in σ bonding ($d_{x^2-y^2}$ and d_{z^2} , in dodecahedral and antiprismatic symmetry, respectively) would be available for π bonding and that 3d sulfur orbitals are not involved in bonding to the metal.^{28,29} Particularly from the stereographic projections in Figure 2 it appears clearly that the most favorable π interaction occurs in the dodecahedral D_{2d} configuration, as much as greater overlap is possible between the metal $d_{x^2-y^2}$ orbital—which is half-filled or filled in vanadium and molybdenum, respectively—and the ligand group orbital of B_1 symmetry formed from the π_a 's, which are empty and are of more appropriate energy than the other π_v orbitals.

In addition, the substantial planarity of the chelating part of the ligands with the phenyl rings (the widest observed angle is 10.71°) suggests further stabilization of the π system as a result of interaction with the antibonding π orbitals of the unsaturated hydrocarbon group.

Aliphatic or arylaliphatic ligands should allow a less effective delocalization of π -electron density. This might be related to the distortions which are observed in the structures of $V(dtpa)_4$ ($T_1T_2 = 87.6^\circ$, $d_t = 0.267 \text{ \AA}$)³⁰ and in one isomer³¹ of $V(CH_3CSS)_4$ ($T_1T_2 = 82.10^\circ$, $d_t = 0.16 \text{ \AA}$), in the

(26) In order of increasing energy the three MO's are of the forms²⁷



(27) See, for example, H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules—An Application of Molecular Orbital Theory," Academic Press, New York, N. Y., 1967, p 463.

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Table IV.^{a,b} Structural parameters for the $M(dtb)_4$ (D_{2d}) Complexes

	Mo(dtb) ₄	V(dtb) ₄ ^e	
		1	2
M-S _A , Å	2.543 (1)	2.56 (2)	
M-S _B , Å	2.475 (1)	2.45 (1)	
R _A /R _B	1.03	1.04	
ϑ_A , deg	37.90 (2)	37.9 (3)	
ϑ_B , deg	75.26 (3)	74.4 (6)	
a, Å	3.124 (1)	3.15 (2)	
m, Å	2.764 (1)	2.79 (2)	
g, Å	3.176 (1)	3.15 (4)	
b, Å	3.612 (1)	3.59 (7)	
T ₁ T ₂ , deg	90.00	90.00	89.6
d _t , Å	?	0.008	0.051
α , deg	0	0	3.6, 2.7
" β "	1.10	1.11	
Space group	$I4_1/a$	$I4_1/a$	
Conventional R	0.033	0.078	
Ref	c	d	

^a Estimated standard deviations in parentheses. For $V(dtb)_4$ the estimated standard deviations have been computed by the use of the formula $\sigma = [\sum_{i=1}^n (x_i - \bar{x})^2 / (n-1)]^{1/2}$, where n is the number of values of x_i and \bar{x} is the mean value (see footnote d). ^b Polyhedron edges and angles are labeled according to ref 21. α is the dihedral angle between the two M-A-B planes within the same trapezoid of the dodecahedron, and d_t is the maximum displacement of the ligand atoms from the best trapezoidal planes. ^c Reference 13. ^d M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Struct. Commun.*, 1, 91 (1972); submitted for publication in *J. Chem. Soc., Dalton Trans.* ^e 1 and 2 indicate the two crystallographically independent molecules in the structure. In 1 the vanadium atom is on the 4 axis; in 2 it is in a general position.

sense that the relative merit of the ligand-ligand repulsion might be increased with respect to $V(dtb)_4$.

For the parameters in Table IV the π -bond strengths of M-S_A and M-S_B are in the ratio 1:1.50 (S_A:S_B), as evaluated by the overlap ratio. π bonding involving S_A atoms is therefore weaker than that with S_B but it is by no means negligible, as is sometimes assumed.

Beyond the choice of stereochemistry, other structural details of the dithiobenzoato complexes are consistent with the proposed π -bonding interactions. (a) The two structures—which have been determined with precision—show no significant difference in the M-S bond lengths, despite the fact that both the covalent and the ionic radii of molybdenum are at least 0.07 Å longer than the corresponding radii for vanadium. Other things being equal, the stronger Mo-S bond is clearly compatible with the availability of two electrons for molybdenum and a single electron for vanadium to occupy the π -bonding molecular orbital arising from the metal $d_{x^2-y^2}$ orbital and the π_a ligand orbital system. (b) There is greater chemical stability of $Mo(dtb)_4$ in solutions of inert or weakly polar solvents, as compared with the corresponding vanadium complex. (c) There is an absence of appreciable twist distortions resulting in dihedral angles between the two bidentates of any one trapezoid, which are required²⁵ by ligand-ligand repulsion energy minimization and which, on the other hand, should lead to a less effective metal and ligand π -orbital overlap.

However, confirmatory structural evidence is not provided by the values of the ϑ_A and ϑ_B angles, which would be expected to be qualitatively increased by π bonding and which are not at all abnormal. Equally, no significant difference is shown by the V-S bond lengths in complexes involving ligands with substituents allowing delocalization of π -electron density to different extents. This would indicate that the π interactions in the dtb complexes are weak but this in itself does not preclude the idea that these interac-

tions influence the stereochemical behavior of the molybdenum(IV) and vanadium(IV) dithiocarboxylates. The general problem is that the detailed structural features of a given eight-coordinate complex are the result of many energy terms, none of which is separately observable since they operate in concert and in opposing ways to produce simply a single observed result. Particularly for the dithiocarboxylate complexes it appears that any understanding of the structural facts must parallel understanding of the unique elec-

tronic structure. In this respect, the electronic spectra of these complexes clearly indicate that any treatment which only includes the metal and ligand ground states cannot provide definite conclusions regarding stereochemistry, bond lengths, and particularly total π -bonding effects.

Registry No. $(\text{TBA})_3\text{MoCl}_6$, 19964-31-9; $(\text{TEA})_3\text{MoCl}_6$, 52175-52-7; $\text{Mo}(\text{dtb})_4$, 52175-53-8; $\text{Mo}(\text{mdtb})_4$, 52175-54-9; $\text{Mo}(\text{dtpa})_4$, 52175-55-0.

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Oxofluoro Complex Anion Equilibria in Aqueous Hydrofluoric Acid. I. Tellurate(IV)

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The hydroxotetrafluorotellurate(IV) anion, $\text{Te}(\text{OH})\text{F}_4^-$, is characterized by Raman and infrared spectroscopy in solid $\text{KTe}(\text{OH})\text{F}_4$ and in aqueous solution. The spectra show that the OH group is in the apical position although there is considerable departure from the spectrum expected for a C_{4v} ion. Raman spectra indicate that aqueous hydrofluoric acid solutions of TeO_2 contain only TeF_5^- and $\text{Te}(\text{OH})\text{F}_4^-$ ions and the equilibrium constant for the hydrolysis of TeF_5^- to $\text{Te}(\text{OH})\text{F}_4^-$ has been estimated. Aqueous solutions of $\text{KTe}(\text{OH})\text{F}_4$ and KTeF_5 show only the spectrum of the $\text{Te}(\text{OH})\text{F}_4^-$ ion.

Introduction

Between the traditional interest in oxo anion behavior in aqueous solutions and, more recently, interest in fluoro anion equilibria in 100% HF,¹ equilibria in aqueous hydrofluoric acid have been comparatively little studied. Moreover, as a general rule, inorganic fluorine chemists exclude water, as far as possible, from systems under study and products showing hydrolysis are avoided. The subject of this series of papers is the fluoro anions formed by the heavier nonmetals of groups V-VII in aqueous hydrofluoric acid and the compounds containing such anions.

Aqueous hydrofluoric acid solutions of Te(VI) have been studied by Kolditz and Fitz,² who found species formed with up to four fluorines coordinated to tellurium. It is interesting that these authors were able to separate the species chromatographically indicating that the compounds formed have considerable kinetic stability. Pentafluorotelluric acid, HOTeF_5 ,³ was not formed, however, in these aqueous solutions.

Prideaux and Millott⁴ and Metzner⁵ in their early studies on solutions of TeO_2 in 40% aqueous hydrofluoric acid isolated some hydrated oxofluoro compounds. Substances with F:Te ratios up to 2:1 were obtained. Pentafluorotellurates, $\text{M}^{\text{I}}\text{TeF}_5$, may be prepared from $\text{M}^{\text{I}}\text{F}$ and TeO_2 in 40% hydrofluoric acid.⁶ Compounds containing the two recently reported fluorotellurate(IV) anions TeOF_4^{2-} and $\text{TeO}_2\text{F}_2^{2-}$ are prepared under anhydrous conditions and cannot be made from aqueous solutions.⁷ This paper concerns

itself with the behavior of Te(IV) in aqueous hydrofluoric acid solutions and the fluorotellurates which may be isolated from such solutions.

Experimental Section

Materials and Apparatus. Tellurium dioxide, 99.9% (Fisher), potassium fluoride, 98% (BDH), and potassium hydrogen carbonate (Analar, BDH) were used directly. Hydrofluoric acid, 50% (J. T. Baker), and perchloric acid (Analar, BDH) were standardized with phenolphthalein as indicator and used directly.

IR spectra were taken as mulls in Nujol, using CsBr plates, on a Beckman IR-20A spectrometer. Raman spectra were recorded on a Jarrell-Ash series 300 spectrometer. A Spectra-Physics argon ion laser was used and detection was by a cooled photomultiplier tube. A spike filter was used to remove plasma lines from the spectra of the solids. Solid samples were contained in 0.5-mm o.d. Pyrex tubes, and, for solutions, a cylindrical sapphire cell 10 cm long and with 5-mm i.d. (Tyco, Sapphikon Division), closed with a plastic cap, was used. Slit widths were 5 cm^{-1} for solid samples and 10 cm^{-1} for solutions. A Raman spectrum of 50% HF showed no bands that interfered with the spectra of the anions studied. Integrated peak intensities of the Raman bands were measured with a planimeter and were accurate to within $\pm 3\%$. All integrated peak intensities were relative to $0.34\text{ M ClO}_4^- = 100$.

The X-ray powder photographs were taken in Lindemann tubes using $\text{Cu K}\alpha$ irradiation. A Debye-Scherrer camera of 11.5-cm diameter was used.

Preparation of the Compounds. $\text{M}^{\text{I}}\text{TeF}_5$. The method of Greenwood, *et al.*,⁶ was used for these preparations.

$\text{KTe}(\text{OH})\text{F}_4$. A 6.4-g amount of TeO_2 (0.040 mol) and 4 g of KHCO_3 (0.040 mol) were weighed into a Teflon dish, and 6.2 ml of 26.0 M hydrofluoric acid was added (0.160 mol). Twenty milliliters of water was added and the mixture was heated to give solution. After filtering to remove traces of suspended material, the solution was allowed to cool. The large crystals which separated were collected by suction filtration and recrystallized from water. The product was dried in a vacuum desiccator over CaCl_2 . *Anal.* Calcd for $\text{KTe}(\text{OH})\text{F}_4$: F, 29.26; Te, 49.13. Found: F, 29.34; Te, 49.14. A second recrystallization proved impossible since dissolution in water was accompanied by some additional hydrolysis. However, dissolution of $\text{KTe}(\text{OH})\text{F}_4$ in a dilute hydrochloric acid solution (Te:Cl = 1:1) yielded back $\text{KTe}(\text{OH})\text{F}_4$ on crystallization indicating the stability of the $\text{Te}(\text{OH})\text{F}_4^-$ anion in dilute acid solution.

The compound was also prepared by forced hydrolysis of KTeF_5 in acetonitrile: $\text{KTeF}_5 + \text{H}_2\text{O} + \text{KF} = \text{KTe}(\text{OH})\text{F}_4 + \text{KHF}_2$. Equimolar amounts of the reactants KTeF_5 , H_2O , and KF were refluxed

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