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## EPR Spectra of Eight-Coordinated Complexes of the Early Transition Metals with Sulfur and Selenium Donor Ligands. 1. Vanadium(IV) and Niobium(IV) Dithiocarboxylates

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Single-crystal EPR studies of V(IV) and Nb(IV) complexes with dithiobenzoic and dithioacetic acid, diluted in the diamagnetic Mo(IV) analogues, are reported. All the compounds are monomeric, eight-coordinate species with geometries intermediate between a triangular dodecahedron and a square antiprism. Two different crystal modifications of the host compound tetrakis(dithioacetato)molybdenum(IV) have been isolated, and the magnetic properties of the vanadium ion, diluted in both, have been investigated. The analysis of the magnetic eigenvalues and eigenvectors indicate that these complexes have a ground-state orbital of the type  $a|x^2 - y^2\rangle - b|z^2\rangle$ . The mixing coefficients  $a$  and  $b$  have been obtained from the experimental results, and their values have been related to the extent of the deviation from the ideal geometries. The vanadium ion, when diluted in the two crystal forms of tetrakis(dithioacetato)molybdenum(IV), gives rise to largely different EPR spectra, thus suggesting different molecular geometries. This result is in keeping with a small energy difference between the two ideal polyhedra. For this reason and for the presence of lattice forces in the solid state (or solvation effects in solution) attempts to relate the detailed geometry of these compounds to the presence of small electronic energy terms can be misleading.

### Introduction

In the last few years several examples of eight-coordinated compounds of the early transition metals with sulfur-containing ligands have been synthesized.<sup>1-7</sup> A large amount of structural<sup>8,9</sup> and theoretical<sup>10</sup> work has appeared on the stereochemical behavior of these complexes.

The ligand-ligand energy repulsion term appears to play the most important role in determining the actual geometry. The potential energy surfaces in the case of eight monodentate or four bidentate equivalent ligands have been calculated by Blight and Kepert.<sup>11,12</sup> Two minima were found, and they correspond to the two most frequently observed eight-coordinate polyhedra, the  $D_{2d}$  triangular dodecahedron (Dod), Figure 1a, and the  $D_{4d}$  square antiprism (SAP), Figure 1b. Further, several authors<sup>6,13</sup> have pointed out the effect of smaller energy terms, such as the electronic structure of the metal ion, the bonding ability of the ligands, and the presence of packing forces, in determining the details of the observed molecular geometry.

Surprisingly, only limited spectroscopic information is available in the literature on these compounds. In this context, EPR spectroscopy provides a convenient tool for distinguishing between eight-coordinated Dod and SAP or lower symmetries along the interconnecting path between the two idealized geometries. In fact the behavior of the  $g$  and  $A$  tensors should allow spectroscopic results to be quantitatively related to crystallographic ones.

With this aim we have carried out a systematic EPR investigation of some selected examples of compounds having these symmetries. This paper reports some results concerning tetrakis(dithiobenzoato)vanadium(IV), V(dtb)<sub>4</sub>, tetrakis(dithiobenzoato)niobium(IV), Nb(dtb)<sub>4</sub>, and tetrakis(dithioacetato)vanadium(IV), V(dta)<sub>4</sub>, substitutionally diluted in single crystals of the diamagnetic Mo(IV) analogues. Un-

fortunately suitable crystals of Nb-doped Mo(dta)<sub>4</sub> could not be grown, and only the powder spectrum has been measured. In addition, two different crystal forms, I and II, of Mo(dta)<sub>4</sub> have been isolated, and the single-crystal EPR spectra of the vanadium ion diluted in both hosts have been obtained. A preliminary report of this work has appeared.<sup>14a</sup>

The work is now being extended to related selenium-containing ligands and, possibly, to analogous complexes of the heavier transition element tantalum.<sup>14b</sup> Hopefully a much more detailed description of the bonding will be possible if hyperfine interaction with the <sup>77</sup>Se isotope is detected. In addition, the greatly different spin-orbit coupling constants of the ligand as well as of the metal ions are expected to affect the spectra strongly.

### Experimental Section

**Reagents.** All manipulations were carried out under dry, oxygen-free nitrogen. Freshly dried solvents were used and degassed immediately before use. The ligands C<sub>6</sub>H<sub>5</sub>CSSH (dtbH)<sup>15</sup> and CH<sub>3</sub>CSSH (dtaH)<sup>16</sup> were prepared according to Houben et al. NbCl<sub>5</sub>, obtained commercially, was purified before use by vacuum sublimation at 100 °C. NbCl<sub>4</sub>(py)<sub>2</sub> was prepared from the pentachloride.<sup>18</sup>

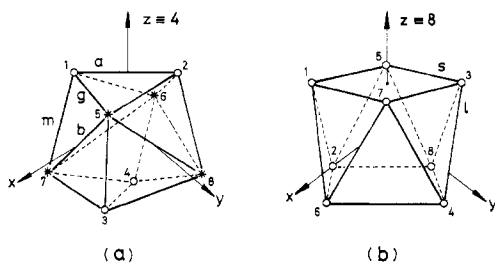
**Preparation of Complexes.** Mo(dtb)<sub>4</sub>,<sup>4</sup> Mo(dta)<sub>4</sub>,<sup>17</sup> V(dtb)<sub>4</sub>,<sup>3</sup> and V(dta)<sub>4</sub><sup>3</sup> were prepared by following previously reported procedures. Nb(dtb)<sub>4</sub>NbCl<sub>5</sub> (1.09 g, 4.02 × 10<sup>-3</sup> mol) was added to a solution of dtbH (3 g, 2.01 × 10<sup>-2</sup> mol) in 70 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred under nitrogen overnight. The resulting red-brown solution was filtered from a yellow-green solid and reduced in volume. On cooling, brown crystals were obtained. Nb(dta)<sub>4</sub>NbCl<sub>4</sub>(py)<sub>2</sub> (1.07 g, 2.72 × 10<sup>-3</sup> mol) was added to a toluene solution of dtaH (1 g, 1.09 × 10<sup>-2</sup> mol) and the mixture was stirred for several days. The resulting solution was filtered and reduced in volume. The compound precipitates as a brown powder on addition of petroleum ether and cooling.

The purity of the compounds was checked by elemental analysis and usual physical measurements.

**Preparation of Doped Crystals.** Suitable single crystals of V/Mo(dtb)<sub>4</sub> and Nb/Mo(dtb)<sub>4</sub> were grown by slow evaporation under nitrogen of CS<sub>2</sub> solutions of the diamagnetic host containing the appropriate quantity of the paramagnetic complex. In the case of V/Mo(dta)<sub>4</sub>, diethyl ether was used as solvent. Crystals of the two

- (1) Bagnall, K. W.; Brown, D.; Holah, D. G. *J. Chem. Soc. A* 1968, 1149.
- (2) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* 1969, 1152.
- (3) Piovesana, O.; Cappuccilli, G. *Inorg. Chem.* 1972, 11, 1543.
- (4) Piovesana, O.; Sestili, L. *Inorg. Chem.* 1974, 13, 2745.
- (5) Nieuwpoort, A.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* 1976, 95, 295.
- (6) Hyde, J.; Zubieta, J. *J. Inorg. Nucl. Chem.* 1977, 39, 289.
- (7) Bereman, R. D.; Nalewajek, D. *J. Inorg. Nucl. Chem.* 1978, 40, 1309.
- (8) Drew, M. G. B. *Coord. Chem. Rev.* 1977, 24, 179.
- (9) Kepert, D. L. *Prog. Inorg. Chem.* 1978, 24, 179.
- (10) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* 1978, 17, 2553.
- (11) Blight, D. G.; Kepert, D. L. *Theor. Chim. Acta* 1968, 11, 51.
- (12) Blight, D. G.; Kepert, D. L. *Inorg. Chem.* 1972, 11, 1556.
- (13) Steffen, W. L.; Fay, R. C. *Inorg. Chem.* 1978, 17, 2120.

- (14) (a) Attanasio, D.; Bellitto, C.; Flamini, A. *Proc. Int. Conf. Coord. Chem., 19th* 1978, 16. (b) Attanasio, D.; Bellitto, C.; Flamini, A., unpublished results.
- (15) Houben, J. *Ber. Dtsch. Chem. Ges.* 1906, 39, 3219.
- (16) Houben, J.; Pohl, H. *Ber. Dtsch. Chem. Ges.* 1907, 40, 1303.
- (17) Piovesana, O., unpublished results.
- (18) Allbut, M.; Feenan, K.; Fowles, G. W. A. *J. Less-Common Met.* 1964, 6, 299.



**Figure 1.** The  $D_{2d}$  triangular dodecahedron (a) and the  $D_{4d}$  square antiprism (b). The molecular axis systems used throughout the text are indicated. In the dodecahedron there are two different ligand sites, forming an elongated tetrahedron (○) and a flattened one (\*). Polyhedral edges are labeled according to Hoard and Silvertown.<sup>31</sup> Different geometrical isomers of the  $M(L-L)_4$  species are indicated through the different edges they span.

modifications I and II could be obtained respectively by cooling at  $-20^\circ\text{C}$  or by slow evaporation of the solution. Attempts to get single crystals of  $Nb/Mo(dta)_4$ , form I or II, failed because of the low solubility of the niobium complex in diethyl ether. Other solvents were used such as  $\text{CS}_2$  or toluene. However, since  $Mo(dta)_4$  is very soluble in these solvents, only microcrystalline powders could be obtained by slow evaporation to dryness. In all cases large concentrations of the paramagnetic complexes (up to 10%) were used to obtain measurable EPR signals.

### Physical Measurements

**Crystallographic Measurements.** Initial unit cell dimensions of  $V/Mo(dta)_4$ , form II, measured at room temperature were obtained from oscillation and zero-layer Weissenberg photographs, taken with  $\text{Cu K}\alpha$  radiation. The same procedure was used to orient single crystals of  $V/Mo(dtb)_4$ ,  $Nb/Mo(dtb)_4$ , and  $V/Mo(dta)_4$ , form I, for the EPR measurements. Removal of the aligned crystals from the X-ray camera to the EPR cavity was accomplished with an accuracy of about  $2^\circ$ .

**EPR Measurements.** All the spectra were recorded at room temperature with an X-band Varian E-9 spectrometer. DPPH ( $g = 2.0036$ ) was used as the reference for measuring the  $g$  values, after the linearity of the field was checked with a  $\text{Mn(II)}$ -doped sample of  $\text{MgO}$ . Single-crystal spectra were measured at  $10^\circ$  intervals in three different planes. The spectra of  $V/Mo(dtb)_4$ ,  $Nb/Mo(dtb)_4$ , and  $V/Mo(dta)_4$ , form I, show only one magnetic site in the unit cell. Therefore information relating the magnetic principal axes to the molecular frame can be obtained only if a well-defined laboratory coordinate system is chosen. Accordingly, the three rotations were performed around the crystal axes. The crystal structure of  $V/Mo(dta)_4$ , form II, is not known. However the angular dependence of the spectra indicates a monoclinic crystal system with two magnetically inequivalent sites in the unit cell. The measurements were referred to a completely arbitrary set of nonperpendicular axes. Afterward the orientations of the magnetic eigenvectors with respect to the monoclinic  $b$  axis were derived.<sup>19</sup>

In all cases rotation data, first analyzed with use of a strong field approximation and a least-squares procedure, were fitted to the complete spin Hamiltonian

$$H_s = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} - g_n \mu_n \mathbf{B} \cdot \mathbf{I}$$

by using a second-order perturbation approach. The spin-Hamiltonian parameters, used to calculate field positions and intensities of each line in each spectrum, were varied until minimization of the function

$$F = [1/N \sum_{i=1}^N (B_{\text{obsd}}^i - B_{\text{calcd}}^i)^2]^{1/2}$$

was achieved. After the last refinements  $F$  was reduced to about 0.05 mT. The summation ran over about 500  $\Delta M_I = 0$  lines. No restrictions were made concerning the relative orientations of the various tensors. Calculations were carried out on a UNIVAC 1108 computer.

Only  $\Delta M_I = 0$  lines were observed. It is well-known<sup>20</sup> that they are rather insensitive to the exact value of the quadrupole coupling tensor, so that only an upper limit could be obtained for  $Q$ . 35-GHz

**Table I.** Experimental and Calculated Field Values (mT) for  $V/Mo(dtb)_4$ , in the Case of Maximum and Minimum  $A_{\text{eff}}$

$H_{\text{exptl}}$	parameters	$H_{\text{calcd}}^{1a}$	parameters	$H_{\text{calcd}}^{2a}$
304.555	$g_{\text{eff}} = 1.9653$	304.28	$g_{\text{eff}} = 1.9639$	304.57
315.710	$A_{\text{eff}}^b = 103.4$	315.45	$A_{\text{eff}}^b = 103.2$	315.74
326.985		326.66		326.93
338.185		337.89		338.15
349.335		349.16		349.41
360.660		360.46		360.69
372.015		371.79		372.01
383.355		383.15		383.36
328.330	$g_{\text{eff}} = 1.9879$	327.18	$g_{\text{eff}} = 1.9814$	328.34
331.425	$A_{\text{eff}}^b = 34.80$	330.30	$A_{\text{eff}}^b = 34.44$	331.42
334.780		333.63		334.74
338.370		337.18		338.28
342.070		340.93		342.04
345.985		344.89		346.00
350.120		349.05		350.15
354.435		353.43		354.49

<sup>a</sup> Starting ( $H_{\text{calcd}}^1$ ) and final ( $H_{\text{calcd}}^2$ ) fields are calculated with a second-order energy expression, by using respectively the magnetic parameter values obtained from the strong field approximation and from the full spin Hamiltonian. <sup>b</sup>  $A_{\text{eff}}$  values are given in units of  $10^{-4} \text{ cm}^{-1}$ .

experiments, which allow direct observation of the forbidden transitions, are in progress and will be published elsewhere.<sup>21</sup>

The relevance of second-order effects in these systems is shown by the results, concerning  $V/Mo(dtb)_4$ , reported in Table I. Initial and final calculated fields are obtained by using the energy expression derived from the full spin Hamiltonian. The  $g$  and  $A$  values obtained from the strong field approximation are used to calculate the initial field values, whereas the final ones correspond to the magnetic parameters modified by the minimization procedure described above.

It turns out that the overall effect of the second-order contributions is to shift all the lines upfield, the maximum shift being reached when the hyperfine splitting reaches its minimum. A large correction has to be applied to the  $g$  values in order to obtain a satisfactory agreement with the experimental spectra. Conversely the hyperfine values undergo only minor changes going from the strong field approximation to the full spin Hamiltonian. The  $g$  value correction can be as high as 30% of the experimental value, i.e.,  $g_i - g_e$ , showing that second-order effects cannot be ignored in these systems.

### Crystal Structures

The crystal and molecular structures of  $Mo(dtb)_4$ ,<sup>22</sup>  $V(dtb)_4$ ,<sup>23</sup>  $Mo(dta)_4$ , form I,<sup>24</sup> and  $V(dta)_4$ ,<sup>25</sup> have been published. No structural information is available for the second crystal modification of  $Mo(dta)_4$  and for the niobium complexes. Some relevant information is summarized in Table II, where the actual coordination sphere of the metal ion is compared with the ideal geometries by means of the  $\delta$  angles<sup>26</sup> and of the parameter  $\Delta$ .<sup>8,27</sup> The reported values are taken from ref 8.

The  $\delta$  angles are the dihedral angles between pairs of triangular faces of the dodecahedron. They are calculated over the four  $b$  edges.  $\Delta$  is defined as the root-mean-square difference between the actual coordinates and those of the ideal polyhedron. This value, minimized by a least-squares procedure, allows different molecules to be compared by using just one parameter.<sup>8</sup>

$Mo(dtb)_4$  and  $V(dtb)_4$  crystallize in the tetragonal space group  $I4_1/a$  but are not isomorphous. The unit cell of  $Mo(dtb)_4$  contains four equivalent monomeric molecules with a regular dodecahedral geometry

(19) Attanasio, D.; Keijzers, C. P.; vandeBerg, J. P.; deBoer, E. *Mol. Phys.* **1976**, *31*, 501.  
(20) White, L. K.; Belford, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 4428.

(21) Attanasio, D.; Bellitto, C.; Flamini, A. *Chem. Phys. Lett.* **1980**, *72*, 307.  
(22) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1975**, 2080.  
(23) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1974**, 1258.  
(24) Dessy, G.; Fares, V.; Scaramuzza, L. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3066.  
(25) Fanfani, L.; Nunzi, A.; Zanazzi, P. F.; Zanzari, A. R. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1298.  
(26) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.  
(27) Dollase, W. A. *Acta Crystallogr., Sect. A* **1974**, *A30*, 513.

Table II. Molecular Geometry and Lattice Parameters of Eight-Coordinate Mo(IV) and V(IV) Dithiocarboxylate Complexes

compd	$\Delta, \text{\AA}$		$\delta$ angles, deg				lattice parameters					ref	
	Dod	SAP					$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$\beta, \text{deg}$	$Z$		space group
Mo(dtb) <sub>4</sub> <sup>a</sup>	0.001	0.165	29.1	29.1	29.1	29.1	21.486		6.73		4	$I4_1/a$	22
V(dtb) <sub>4</sub> <sup>b</sup>	0.003	0.161	30.3	30.0	30.3	30.3	47.887		6.72		20	$I4_1/a$	23
	0.024	0.178	25.6	32.3	33.3	33.6							
Mo(dta) <sub>4</sub> , form I			17.7	17.7	50.3	50.3	9.616	8.706	12.539	126.47	2	$P2/c$	24
Mo(dta) <sub>4</sub> , form II							13.2	9.5	7.0 or 14.0	96		monoclinic	this work
V(dta) <sub>4</sub> <sup>b</sup>	0.011	0.181	33.6	33.6	34.7	35.8	13.36	8.09	16.41	114.0	4	$P2/c$	
	0.098	0.122	17.7	17.7	33.1	43.2							
Dod <sup>c</sup>			29.5	29.5	29.5	29.5							
SAP <sup>c</sup>			0.0	0.0	52.4	52.4							

<sup>a</sup> Tabulated  $\Delta$  values are from ref 8. <sup>b</sup> Two independent molecules, with different  $\Delta$  and  $\delta$  angles, are present in the unit cell of the indicated compounds. <sup>c</sup> The reported  $\delta$  values are those required from the so-called hard-sphere model (HSM). Symmetry requires only four identical values (Dod) or two zero and two equivalent values (SAP).

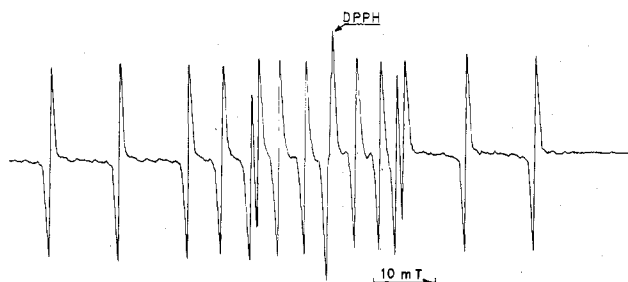


Figure 2. X-Band EPR spectrum of a single crystal of Nb/Mo(dtb)<sub>4</sub> at 300 K for a general orientation of  $B_0$ .

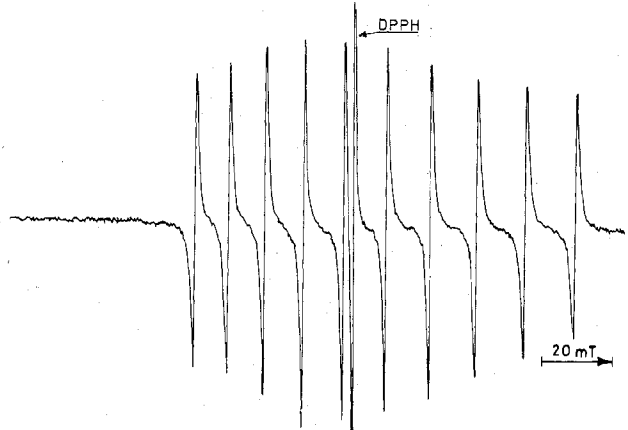


Figure 3. X-Band EPR spectrum of a single crystal of V/Mo(dta)<sub>4</sub>, form II, at 300 K.  $B_0$  lies along the [001] direction.

(subclass  $D_{2d}$ ,  $m\bar{3}m$ ). The coordination polyhedra have their  $\bar{4}$  axes parallel to the [001] direction.

Two crystallographically independent, but strictly similar, molecules are present in the unit cell of V(dtb)<sub>4</sub>. The shape parameters of Table II indicate that one of the molecules is slightly distorted with respect to the ideal dodecahedral geometry. The EPR results will show that the vanadium ions, as well as the niobium ions, accept the almost ideal geometry of the diamagnetic host.

Mo(dta)<sub>4</sub>, form I, crystallizes in the monoclinic space group  $P2/c$ . The structure consists of discrete molecules, which can be described as triangular dodecahedra (isomer  $m\bar{3}m$ ) significantly distorted toward square antiprisms (isomer  $ssss$ ). There are two Mo(dta)<sub>4</sub> molecules in the unit cell, each Mo(IV) ion lying on the twofold axis. The coordination polyhedron has its pseudo  $\bar{4}$  axis parallel to the (101) plane, at ca.  $135^\circ$  from the  $a$  axis.

V(dta)<sub>4</sub> crystallizes in the same space group  $P2/c$ . Its unit cell contains two nonequivalent molecules, which are different dodecahedral stereoisomers. One of the two molecular units has a unique geometry intermediate between the Dod  $m\bar{3}m$  and the SAP  $ssss$  isomers. The second one has the "usual", quite regular Dod  $m\bar{3}m$  geometry.

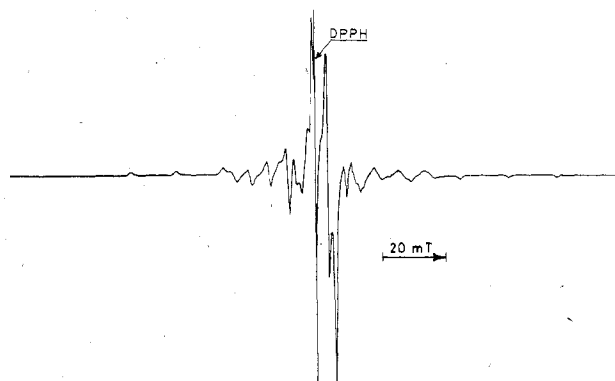


Figure 4. X-Band powder spectrum of V/Mo(dta)<sub>4</sub>, form I, at 300 K.

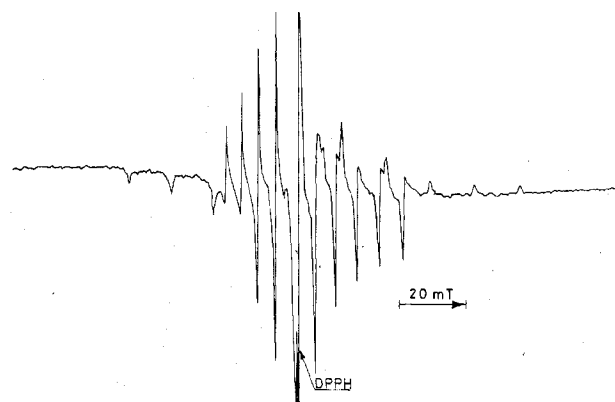


Figure 5. X-Band EPR spectrum of Nb/Mo(dtb)<sub>4</sub> at 300 K.

## Results

Representative spectra of the complexes investigated are reported in Figures 2–5. In agreement with the X-ray results V/Mo(dtb)<sub>4</sub>, Nb/Mo(dtb)<sub>4</sub>, and V/Mo(dta)<sub>4</sub>, form I, exhibit only one set of eight or ten lines (<sup>51</sup>V(100%),  $I = 7/2$ ; <sup>93</sup>Nb(100%),  $I = 9/2$ ).

In the case of V/Mo(dta)<sub>4</sub>, form II, a pair of resonances from magnetically inequivalent molecules is observed. There is only one plane of equivalence of the two signals. Since the tensors are rhombic and their components have different orientations for the inequivalent sites, the monoclinic symmetry of the host crystal is confirmed.<sup>28</sup>

The principal values of the tensors are listed in Tables III and IV respectively for the vanadium and niobium complexes.

**Table III.** Spin-Hamiltonian Parameters of the Vanadium Dithiocarboxylate Complexes at 300 K<sup>a,b</sup>

principal axes	V/Mo(dtb) <sub>4</sub>	V/Mo(dta) <sub>4</sub> , form II	V/Mo(dta) <sub>4</sub> , form I
<i>g</i> <sub>1</sub>	1.9816 ± 0.0001	1.9817 ± 0.0001	1.9889 ± 0.0001
<i>g</i> <sub>2</sub>	1.9814 ± 0.0001	1.9778 ± 0.0002	1.9735 ± 0.0002
<i>g</i> <sub>3</sub>	1.9632 ± 0.0003	1.9610 ± 0.0003	1.9604 ± 0.0003
<i>g</i> <sub>av</sub>	1.9754	1.9735	1.9743
<i>g</i> <sub>iso</sub> <sup>c</sup>	1.976 ± 0.001	1.977 ± 0.001	1.977 ± 0.001
<i>A</i> <sub>1</sub>	104.9 ± 0.3	107.3 ± 0.4	103.8 ± 0.4
<i>A</i> <sub>2</sub>	34.50 ± 0.1	43.0 ± 0.2	55.3 ± 0.2
<i>A</i> <sub>3</sub>	34.45 ± 0.1	31.3 ± 0.2	24.0 ± 0.2
<i>A</i> <sub>av</sub>	58.95	60.5	61.0
<i>A</i> <sub>iso</sub> <sup>c</sup>	59.0 ± 0.5	61.2 ± 0.5	61.2 ± 0.5
<i>Q</i> <sub>1</sub>	0.3	0.3	0.3

<sup>a</sup> Hyperfine and quadrupole splittings are in units of 10<sup>-4</sup> cm<sup>-1</sup>.<sup>b</sup> The signs of the hyperfine tensor principal values are discussed in the text. <sup>c</sup> From solution spectra in toluene at 300 K.**Table IV.** Spin-Hamiltonian Parameters of the Niobium Dithiocarboxylate Complexes at 300 K<sup>a,b</sup>

principal axes	Nb/Mo(dtb) <sub>4</sub>	Nb/Mo(dta) <sub>4</sub> , form II <sup>c</sup>
<i>g</i> <sub>1</sub>	1.9737 ± 0.0002	1.977 ± 0.001
<i>g</i> <sub>2</sub>	1.9734 ± 0.0002	1.973 ± 0.001
<i>g</i> <sub>3</sub>	1.9597 ± 0.0003	1.952 ± 0.001
<i>g</i> <sub>av</sub>	1.9689	1.967
<i>g</i> <sub>iso</sub> <sup>d</sup>	1.967 ± 0.001	1.965 ± 0.001
<i>A</i> <sub>1</sub>	119.5 ± 0.3	138.5 ± 0.5
<i>A</i> <sub>2</sub>	54.7 ± 0.1	64.5 ± 0.5
<i>A</i> <sub>3</sub>	54.5 ± 0.1	57.5 ± 0.5
<i>A</i> <sub>av</sub>	76.2	86.8
<i>A</i> <sub>iso</sub> <sup>d</sup>	75.5 ± 0.5	87.5 ± 0.5
<i>Q</i> <sub>1</sub>	0.3	

<sup>a</sup> Hyperfine and quadrupole splittings are in units of 10<sup>-4</sup> cm<sup>-1</sup>.<sup>b</sup> The signs of the hyperfine tensor principal values are discussed in the text. <sup>c</sup> Powder spectrum. <sup>d</sup> From solution spectra in toluene at 300 K.

The three vanadium species have rather similar spin-Hamiltonian parameters. The relationship  $g_3 < g_1 \approx g_2$  strongly indicates, for all of them, an essentially  $|x^2 - y^2\rangle$  ground-state orbital, in agreement with a more or less distorted dodecahedral geometry.<sup>29</sup>

As far as the signs of the hyperfine principal values are concerned, comparison of the solution isotropic splittings with the average values led to the conclusion that all the principal values had the same sign. In agreement with the spin-polarization mechanism<sup>30</sup> the *A*<sub>iso</sub> values were taken to be negative, and the same sign was given to the principal values of the hyperfine coupling tensors.

The most important difference between the three compounds is the extent of the rhombic distortion. The spectrum of V/Mo(dtb)<sub>4</sub> is almost perfectly axial. Differences between *g*<sub>1</sub> and *g*<sub>2</sub> and *A*<sub>2</sub><sup>V</sup> and *A*<sub>3</sub><sup>V</sup> are respectively 0.0001 × 10<sup>-4</sup> and 0.05 × 10<sup>-4</sup> cm<sup>-1</sup>, i.e., of the order of the experimental errors.

The two crystal modifications V/Mo(dta)<sub>4</sub>, forms II and I, exhibit an increasing rhombic distortion. The perpendicular Δ*g* values are 0.004 and 0.015. The corresponding Δ*A*<sup>V</sup> values are 11.7 × 10<sup>-4</sup> and 31.3 × 10<sup>-4</sup> cm<sup>-1</sup>.

The magnetic eigenvectors have been related to the molecular geometry only in the case of V/Mo(dtb)<sub>4</sub> and V/Mo(dta)<sub>4</sub>, form I, for which complete structural information is available.

In the case of V/Mo(dtb)<sub>4</sub> the parallel *g* and *A*<sup>V</sup> directions have been found to lie along the [001] crystal direction, i.e.,

**Table V.** Experimental Angles (Deg) Formed by the Magnetic Eigenvectors and by the Dod Symmetry Axes with Respect to the Crystal Axis System of V/Mo(dta)<sub>4</sub>, Form I

	<i>a</i>	<i>b</i>	<i>c</i> <sup>a</sup>
<i>g</i> <sub>1</sub>	74.7	163.4	81.0
<i>g</i> <sub>2</sub>	54.3	89.3	144.3
<i>g</i> <sub>3</sub>	141.0	83.5	55.8
<i>A</i> <sub>1</sub>	142.0	83.2	57.2
<i>A</i> <sub>2</sub>	55.4	89.5	145.4
<i>A</i> <sub>3</sub>	76.5	163.2	80.2
<i>S</i> <sub>4</sub>	139.0	90.0	49.0
<i>C</i> <sub>2</sub> <sup>'</sup>	90.0	0.0	90.0
<i>C</i> <sub>2</sub> <sup>''</sup>	49.0	90.0	41.0

<sup>a</sup> The *c*' direction is given by the cross product between *a* and *b*.**Table VI.** Experimental Angles (Deg) between the Magnetic Eigenvectors and the Monoclinic Symmetry Axis (*b*) in V/Mo(dta)<sub>4</sub>, Form II

<i>g</i> <sub>1</sub>	<i>g</i> <sub>2</sub>	<i>g</i> <sub>3</sub>	<i>A</i> <sub>1</sub>	<i>A</i> <sub>2</sub>	<i>A</i> <sub>3</sub>
78	54	39	38	58	71

along the  $\bar{4}$  dodecahedral axis.

Table V lists the experimental angles between the *g* and *A*<sup>V</sup> principal directions and the crystal axis system of V/Mo(dta)<sub>4</sub>, form I. The angles that the dodecahedral symmetry axes form with the same reference frame are also reported for comparison. It turns out that, in spite of the low symmetry of this compound, the *g* and hyperfine axes are almost coincident and approximately directed along the symmetry axes of the ideal dodecahedron. *A*<sub>1</sub><sup>V</sup> and *g*<sub>3</sub>, which lie along the  $\bar{4}$  direction, are assigned as the *z* components. The small discrepancies, which can be found in the results of Table V, are probably due to experimental errors. The EPR measurements have been carried out in an arbitrary reference frame, simply related to the crystal morphology, and then converted to the *abc*' frame with the aid of a Euler transformation ( $\alpha = \gamma = 0^\circ$ ,  $\beta = 28^\circ$ ).

In the case of V/Mo(dta)<sub>4</sub>, form II, in the absence of full structural information, the EPR experiment gives only the orientations of the magnetic eigenvectors with respect to the monoclinic axis (Table VI). However, from the above results, it seems reasonable to assume that also for this compound the magnetic and dodecahedral axes coincide.

The magnetic eigenvalues and eigenvectors of the niobium complexes are in line with the results discussed above. The powder spectrum of the Nb/Mo(dta)<sub>4</sub> system indicates that the host compound is the crystal modification II, in agreement with the method used to prepare the sample.

The molecular geometry of Mo(dta)<sub>4</sub>, form I, has been described as being midway between the square-antiprismatic and the dodecahedral limits. In spite of this our results imply that in all cases the effective crystal field experienced by the paramagnetic ion can be described as a strong *D*<sub>2d</sub> perturbation with a superimposed small low-symmetry field.

## Discussion and Conclusions

The most symmetric pathway connecting Dod to SAP maintains the molecule in *D*<sub>2</sub> symmetry. In this situation only two independent  $\delta$  angles exist, steadily changing from 29.5° to 0.0° and 52.4°. For example the molecular geometry of the lowest symmetry modification of Mo(dta)<sub>4</sub>, i.e., form I, is described by  $\delta$  and  $\delta'$ , respectively equal to 17.7 and 50.3°. Even if distortions are present, which lower the molecular symmetry below *D*<sub>2</sub>, the choice of this point group allows the main low-symmetry effect, i.e., configuration interaction among states belonging to the same irreducible representation, to be accounted for.

In *D*<sub>2</sub> symmetry the ground-state function of a d<sup>1</sup> system can be written as eq 1 with  $a^2 + b^2 = 1$ . Since  $0 \leq a \leq 1$  this

$$\psi_g = a|x^2 - y^2\rangle - b|z^2\rangle \quad (1)$$

(29) McGarvey, B. R. *Transition Met. Chem.* **1966**, 3, 89.(30) McGarvey, B. R. *J. Phys. Chem.* **1967**, 71, 51.(31) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, 2, 235.

Table VII. Best-Fit Parameters from the Analysis of  $g$  and Hyperfine Principal Values<sup>a</sup>

compd	$a$	$b$	$b^2/b^2_{SAP}, \%$	$P$	$K$	$\lambda/\Delta_{xy}$	$\lambda/\Delta_{xz}$	$\lambda/\Delta_{yz}$
V/Mo(dtb) <sub>4</sub>	0.9999	0.0005	0	79.3	55.8	0.0049	0.0104	0.0104
Nb/Mo(dtb) <sub>4</sub>	0.9999	0.001	0	73.0	73.8	0.0053	0.0144	0.0144
V/Mo(dta) <sub>4</sub> , form II	0.9972	0.075	2	79.6	58.3	0.0052	0.0096	0.0137
Nb/Mo(dta) <sub>4</sub> , form II	0.9992	0.039	1	86.5	83.8	0.0064	0.0129	0.0146
V/Mo(dta) <sub>4</sub>	0.9798	0.200	16	78.0	58.8	0.0055	0.0082	0.0167

<sup>a</sup>  $P$  and  $K$  values are in units of  $10^{-4} \text{ cm}^{-1}$ . The limiting  $a$  and  $b$  values are respectively  $a_{D_{od}} = 1$ ,  $b_{D_{od}} = 0$ ,  $a_{SAP} = 3/2$ , and  $b_{SAP} = 0.5$ .  $\Delta_i$  means  $\Delta E_{|x^2-y^2\rangle \rightarrow |i\rangle}$ .

function represents the  $|x^2 - y^2\rangle$  and  $|z^2\rangle$  states and all possible mixtures.

Here only d-type orbitals will be considered so that the effects of covalency will be given indirectly by the modified values of the spin-orbit and  $\langle r^{-3} \rangle$  parameters. No attempt has been made to allow mixing of function 1 with linear combination of the ligand orbitals and to derive the corresponding MO coefficients. The results of such calculation strongly depend on the choice of the parameters  $\lambda$  and  $\langle r^{-3} \rangle$ , which seems to be largely a matter of taste. Very different values had been used in the literature, so that MO coefficients calculated by different authors cannot usually be compared and appear to be of little value.

In order to understand the significance of the wave function  $\varphi_g$ , it must be realized that  $a = 1$  or  $b = 1$  represents the ground-state orbitals for dodecahedral or square-antiprismatic symmetry in the coordinate systems of Figure 1a,b. However, if we take into account intermediate geometries, we must refer to the same frame, for instance, that of Figure 1a. Therefore, the ground-state orbital for a square-antiprismatic coordination is given by  $a = 3^{1/2}/2$  and  $b = 1/2$ , which corresponds to the  $|3x^2 - r^2\rangle$  orbital. Starting with the zeroth order expression,  $\varphi_g$  mixing of excited states through spin-orbit interaction must be considered. Expressions for the spin-Hamiltonian parameters can then be found by standard procedures, applying the Zeeman and hyperfine operators. The final equations (eq 2 and 3) are essentially those derived by McGarvey,<sup>29</sup> where  $P = g_e g_n \mu_b \mu_n \langle r^{-3} \rangle$ ,  $K = -g_e g_n \mu_b \mu_n (2/3\lambda)$ ,  $\Delta g_i = g_e - g_i$ , and  $\Delta_i = \Delta E_{|x^2-y^2\rangle \rightarrow |i\rangle}$ .

$$\begin{aligned}
 g_z &= g_e - 8a^2\lambda/\Delta_{xy} & g_x &= g_e - 2(a - 3^{1/2}b)^2\lambda/\Delta_{yz} \\
 g_y &= g_e - 2(a + 3^{1/2}b)^2\lambda/\Delta_{xz} & & \\
 A_z &= -K + P \left[ -\frac{4}{7}(a^2 - b^2) - \frac{1}{14} \left( \frac{3a - 3^{1/2}b}{a + 3^{1/2}b} \right) \Delta g_y - \right. \\
 & \quad \left. \frac{1}{14} \left( \frac{3a + 3^{1/2}b}{a - 3^{1/2}b} \right) \Delta g_x - \Delta g_z \right] \\
 A_x &= -K + P \left[ \frac{2}{7}(a^2 - b^2) + \frac{4(3^{1/2})}{7}ab - \Delta g_x + \right. \\
 & \quad \left. \frac{1}{14} \left( \frac{3a - 3^{1/2}b}{a + 3^{1/2}b} \right) \Delta g_y + \frac{1}{7} \frac{b}{a} \Delta g_z \right] \\
 A_y &= -K + P \left[ \frac{2}{7}(a^2 - b^2) - \frac{4(3^{1/2})}{7}ab - \Delta g_y + \right. \\
 & \quad \left. \frac{1}{14} \left( \frac{3a + 3^{1/2}b}{a - 3^{1/2}b} \right) \Delta g_x - \frac{1}{7} \frac{b}{a} \Delta g_z \right]
 \end{aligned} \quad (2)$$

With the aid of the above expressions an analysis of the A-tensor anisotropy has been carried out. The  $a$ ,  $b$ ,  $K$ , and  $P$  values listed in Table VII have been obtained by solving the system of the three hyperfine equations plus the normalization condition by means of an iterative procedure.

The reason for focusing the analysis mainly on the hyperfine tensor is twofold. First, although the optical spectra of some of the compounds investigated have already been reported,<sup>3</sup> satisfactory explanation of their ligand field transitions seems still to be lacking. Second, it should be remembered that the  $g$ -tensor anisotropy is the consequence of some orbital angular momentum reintroduced into the ground state by the spin-orbit interaction. Therefore such anisotropy is affected by the symmetry of the overall electric charge distribution. Conversely, the hyperfine coupling is a magnetic interaction between the metal nucleus and the unpaired spin distribution only. Its anisotropy is primarily determined by the symmetry of the unpaired electron molecular orbital.

The calculated  $a$  and  $b$  values indicate that the ground-state MO is an A-type orbital essentially composed of  $|x^2 - y^2\rangle$  with some amount of  $|z^2\rangle$ . In the case of the vanadium and niobium dtb complexes the  $|z^2\rangle$  contribution is almost zero, as expected for a virtually ideally dodecahedral symmetry. The increasing  $b$  values displayed by the three vanadium and niobium dta compounds suggest the presence of an increasing low-symmetry perturbation due to the fact that the structure of these complexes is somewhere in between the two ideal geometries.

A measure of the degree of this perturbation is given by the  $b^2$  values. In the case of V/Mo(dta)<sub>4</sub>, form I, the  $|z^2\rangle$  admixture is 16% of that required by an ideal antiprismatic symmetry. The corresponding values for Nb- and V/Mo(dta)<sub>4</sub>, form II, are much lower, i.e., 1% and 2%. These results indicate that crystal packing forces in the solid state, or solvation effects in solution, may have a large influence and may easily overcome the effect of small electronic energy terms in determining the stereochemical behavior of these eight-coordinate species. For instance, the regular  $D_{2d}$  symmetry of Mo(dtb)<sub>4</sub>, with respect to the distorted geometry of the single previously known crystal modification of Mo(dta)<sub>4</sub>, form I, has been tentatively ascribed to  $\pi$ -bonding effects.<sup>8</sup> According to this reasoning, the presence of the phenyl groups, which are almost coplanar with the chelate rings of the dtb ligand, should stabilize the molecular system, thus strengthening the d- $\pi$  bonding. In the case of Mo(IV),  $d^2$ , the stabilizing interaction between the metal  $|x^2 - y^2\rangle$  and the ligand  $\pi^*$  orbitals should be favored by dodecahedral rather than antiprismatic structures.<sup>10</sup> These arguments would explain the different geometries of the two molybdenum complexes. However, the synthesis of Mo(dta)<sub>4</sub>, form II, and the analysis of the EPR properties of its V-doped crystals, pointing to an almost undistorted  $D_{2d}$  symmetry, indicate that  $\pi$  bonding is a minor effect, which can be completely "swamped" by solid-state forces. In conclusion, since the role of such small electronic factors is extremely difficult to assess experimentally, any rationalization of the observed geometries on this basis is highly speculative.

In addition to the best-fit mixing coefficients  $a$  and  $b$ , Table VII gives also the corresponding values of the isotropic and anisotropic hyperfine terms  $K$  and  $P$ .

The calculated  $K$  values agree satisfactorily with the experimental  $A_{av}$  values, keeping in mind that these two quantities are related by the expression<sup>30</sup>  $A_{av} = -K + (g_{av} - g_e)P$ . All the V and Nb complexes have rather similar  $A_{av}$  values.

The magnitude of the isotropic splitting is mainly due to a negative contribution from the spin polarization of the inner-shell *s* electrons. However, since a small admixture of the 4*s* (or 5*s*) orbital into the ground state would yield a positive contribution to  $A_{av}$ , we would expect the less-symmetry compounds, i.e., the dta complexes, to have smaller absolute values of  $A_{av}$ . Inspection of Tables III and IV shows the opposite trend. We have no readily available explanation for this. As a matter of fact, such a result would imply that the dta complexes give rise to larger spin-polarization contributions. However, although possible, this is unlikely to happen in compounds with very similar electronic structure and metal-ligand bond covalency. The best-fit  $P$  values of Table VII are strongly reduced with respect to the free-ion values. The metal d-orbital contribution accounts for about half of the total spin density, thus suggesting strong delocalization of the unpaired electron in these compounds. Theoretical  $P$  values for different electronic configurations of the vanadium atom have been computed from Hartree-Fock ( $r^{-3}$ ) values:<sup>30</sup> V ( $d^5$ ),  $85.7 \times 10^{-4}$ ; V<sup>+</sup> ( $d^4$ ),  $107 \times 10^{-4}$ ; V<sup>2+</sup> ( $d^3$ ),  $128 \times 10^{-4}$ ; V<sup>3+</sup> ( $d^2$ ),  $150 \times 10^{-4}$ ; V<sup>4+</sup> ( $d^1$ ),  $172 \times 10^{-4} \text{ cm}^{-1}$ . Comparison with our experimental results indicate a near-zero effective nuclear charge at the vanadium atom.

The effective spin-orbit coupling parameters of our systems can be estimated from the  $g$ -value expressions given before, provided that the energies of the d-d transitions are known. The electronic spectra of V(dtb)<sub>4</sub> and V(dta)<sub>4</sub> have been reported,<sup>3</sup> but their ligand field transitions could not be assigned, and we have recorded the diffuse reflectance spectrum of Nb(dtb)<sub>4</sub>.

In the region from  $10$  to  $25 \times 10^3 \text{ cm}^{-1}$  solid V(dtb)<sub>4</sub> shows absorptions at  $11.8$ ,  $15.2$ ,  $16.2$ ,  $18.8$ , and  $22.2 \times 10^3 \text{ cm}^{-1}$  as shoulders on the tail of a very high-intensity broad absorption in the near-UV region. A value of  $110 \text{ cm}^{-1}$  for  $\lambda$  leads to calculated electronic energies of  $10.6 \times 10^3 \text{ cm}^{-1}$  for  $|x^2 - y^2\rangle \rightarrow |xz\rangle$ ,  $|yz\rangle$  and of  $22.5 \times 10^3 \text{ cm}^{-1}$  for  $|x^2 - y^2\rangle \rightarrow |xy\rangle$ . This is the only possible fitting on the basis of the EPR results, and the probable ordering of the d-level energies is  $|x^2 - y^2\rangle < |xz\rangle$ ,

$|yz\rangle < |z^2\rangle < |xy\rangle$ .

The solid-state optical spectrum of V(dta)<sub>4</sub> is complicated by the presence of two largely different molecules in the unit cell. However, since the unique crystal and molecular structure of V(dta)<sub>4</sub> has been ascribed to the presence of strong packing forces, we feel that the geometries of V/Mo(dta)<sub>4</sub>, form II, and V(dta)<sub>4</sub> in solution are not too different, so that optical and EPR data from these two systems can be compared. The solution spectrum of V(dta)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> shows absorptions at  $12.8$ ,  $19.2$ , and  $21.7 \times 10^3 \text{ cm}^{-1}$ . The best fit of the  $g$ -value expressions to these energies gives  $\lambda = 115 \text{ cm}^{-1}$ ,  $|x^2 - y^2\rangle \rightarrow |yz\rangle = 8.5 \times 10^3 \text{ cm}^{-1}$ ,  $|x^2 - y^2\rangle \rightarrow |xz\rangle = 12 \times 10^3 \text{ cm}^{-1}$ , and  $|x^2 - y^2\rangle \rightarrow |xy\rangle = 22.2 \times 10^3 \text{ cm}^{-1}$ . The two calculated high-energy values compare favorably with the two experimental absorptions, whereas no low-energy transition has been detected. A more symmetric geometry of V(dta)<sub>4</sub> in solution, with respect to V/Mo(dta)<sub>4</sub>, form II, can account for this, although the failure to detect a low-energy broad and weak absorption is still a possibility.

The diffuse reflectance spectrum of Nb(dtb)<sub>4</sub> shows absorptions at  $9.0$ ,  $10.3$ ,  $15.2$ ,  $19.2$ , and  $21.1 \times 10^3 \text{ cm}^{-1}$ . A value of  $123 \text{ cm}^{-1}$  for  $\lambda$  gives  $|x^2 - y^2\rangle \rightarrow |xz\rangle$ ,  $|yz\rangle = 8.6 \times 10^3 \text{ cm}^{-1}$ , and  $|x^2 - y^2\rangle \rightarrow |xy\rangle = 23.2 \times 10^3 \text{ cm}^{-1}$ . The d-level ordering is the same as suggested for V(dtb)<sub>4</sub>.

All the  $\lambda$  values calculated above are much smaller than the corresponding free-ion values and are in line with the strong covalency suggested by the calculated  $P$  values. In particular the  $\lambda$  values calculated for the Nb complexes suggest a much more extensive delocalization of the electron spin density for these compounds than for their V counterparts.

**Registry No.** Nb(dtb)<sub>4</sub> (salt form), 74752-80-0; Nb(dtb)<sub>4</sub> (coordination form), 74752-83-3; Nb(dta)<sub>4</sub> (salt form), 74752-81-1; Nb(dta)<sub>4</sub> (coordination form), 74752-82-2; Mo(dtb)<sub>4</sub> (salt form), 57956-15-7; Mo(dtb)<sub>4</sub> (coordination form), 52175-53-8; V(dtb)<sub>4</sub> (salt form), 32690-40-7; V(dtb)<sub>4</sub> (coordination form), 31871-44-0; Mo(dta)<sub>4</sub> (salt form), 68538-10-3; Mo(dta)<sub>4</sub> (coordination form), 68340-66-9; V(dta)<sub>4</sub> (salt form), 32690-39-4; V(dta)<sub>4</sub> (coordination form), 31871-43-9; Nb(py)<sub>2</sub>Cl<sub>4</sub>, 42941-81-1.