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Eight-Coordination. 3.[1] Dithiobenzoato Complexes of Titanium(IV) and Vanadium(V) with High Coordination Numbers

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In order to gain further understanding of the role of π bonding in eight-coordinate transition-metal complexes involving four symmetrical bidentate ligands, we have investigated the dithiobenzoic acid (dtbH) derivatives of titanium(IV) and vanadium(V). Compounds of the type VO(dtb)$_3$ and Ti(dtb)$_n$Cl$_{4-n}$ (n = 2, 3, or 4) have been isolated in a variety of conditions. Coordination numbers of 6, 7, and 8, for the species containing 2, 3, and 4 dtb ligands, respectively, have been inferred from infrared spectra and molecular weight and conductivity measurements. The electronic structure of the compounds, as revealed by their UV-visible spectra, is discussed and related to those of known dithiocarboxylato and dithiocarbamato eight-coordinate species with d^0, d^1, and d^2 configurations. It is concluded that π-bonding interactions of dtb with d^0 systems are much less effective than with d^1 and d^2 systems. The opposite situation occurs in the corresponding dithiocarbamato complexes.

Introduction[2]

The relative merit of the factors which can influence the formation, the stability, and the stereochemical behavior of an eight-coordinate species is a topic which has received a great deal of attention.[3-7]

The importance of π-bonding and π-antibonding interactions has been mainly emphasized in connection with the stereochemical configurations adopted by molecules of type MX$_4$Y$_4$ (M = transition metal, X = π donor, Y = π acceptor).[3,5,8-10] The role of π interactions in compounds involving four symmetrical bidentate ligands, M(A-A)$_4$, is much less documented. Most of the M(A-A)$_4$ structures appear to be determined primarily by ligand-ligand repulsion energies,[11] and it is generally assumed that, in them, the π-bonding energy term is overwhelmed. Eight-coordinate transition-metal dithiocarbamates and dithiocarboxylates are noteworthy in this regard. They show structures[12] which do not corroborate predictions based on ligand-ligand repulsion energy arguments and which differ markedly between themselves in spite of the uniform "bite"[21] (1.10-1.11), C-S, MSC, and SCS bond lengths and angles. Marked differences[1,22-24] in stability, electronic spectra, redox potentials, etc. parallel the stereochemical variations.

In an attempt to rationalize the properties of the dodecahedral dtb complexes of vanadium(IV) (d^1) and molybdenum(IV) (d^2), we suggested[1] a nonnegligible role of the lowest empty π-antibonding MO's of the ligand system. In order to gain further evidence of the role of π bonding in compounds of this type, we have now investigated the dithiobenzoic acid derivatives of titanium(IV), a d^0 system with d orbitals at approximately the same energy as molybdenum(IV) and vanadium(IV) and with covalent and ionic radii very close to those of molybdenum(IV). In view of the unusual reactions given by the R-CS$_2^-$ ligands with the VO^{2+} ion[25], the ligation ability of dtb toward oxovanadium(V) has also been investigated. No previous examples of dithio acid derivatives of titanium(IV) or vanadium(V) appear to have been reported in the literature. On the contrary, the dtc complexes of these metal ions have received considerable attention.[13,26-30]

Experimental Section

VOCl$_3$, VCl$_3$, VOCl$_2$, and TiCl$_4$. These compounds were obtained commercially and were used as received.

Ligands. dtbH,[31] p-CH$_3$OC$_6$H$_4$CSSH,[32] their sodium salts, and Zn(C$_6$H$_5$CS$_2$S)$_2$[33] were prepared by following known procedures.

Preparations. All the syntheses were performed under anhydrous conditions in a dry nitrogen atmosphere.

VO(dtb)$_3$. (a) This compound can be obtained very easily by adding a 0.5 M solution of VOCl$_3$ in absolute ethanol to a saturated solution of dtbNa in the same solvent. A light brown powder is immediately formed, in almost quantitative yield; mp ~116 °C dec. Bright yellow needles, mp 120-121 °C dec, were obtained upon crystallization from acetonitrile. Anal. Calcd for C$_{21}$H$_{15}$S$_6$VO: C, 47.89; H, 2.88; S, 36.52; V, 9.67; O, 3.04. Found: C, 47.88; H, 3.03; S, 37.41; V, 10.31; O, 3.28.

(b) A 0.5 M solution of VOCl$_2$ in acetonitrile was added dropwise, with stirring, to a saturated solution of Zn(C$_6$H$_5$CS$_2$S)$_2$ in acetonitrile (~2 mmol in 50 mL). The addition caused the formation of a brown-yellow precipitate and was continued until no more solid separated. The solid was recrystallized from acetonitrile: 0.20 g; mp 122 °C dec.

(c) Reaction between Zn(C$_6$H$_5$CS$_2$S)$_2$ and VCl$_3$ (which is known to be oxidized to V(IV) by dtbH[25]) yielded V(dtb)$_4$ instead of the expected VO(dtb)$_3$. Upon addition of a VCl$_3$ solution in absolute ethanol (0.8 mmol in 30 mL) to a dichloromethane solution of Zn(C$_6$H$_5$CS$_2$S)$_2$ (4.6 mmol in 40 mL) and subsequent cooling of the solution at -10 °C overnight, dark red crystals were obtained. Their resultant physical properties are identical with those of the already known V(dtb)$_4$.[25]

Ti(dtb)$_2$Cl$_2$. This was obtained by heterogeneous reaction between 2 mmol of anhydrous dtbNa and 8 mmol of TiCl$_4$ in 15 mL of dichloromethane. After the mixture stood for ~12 h at room temperature, it was filtered under vacuum. The volume of the filtrate was then reduced to ~5 mL by vacuum distillation. Upon cooling of the final solution at -10 °C, deep red needles separated. These were filtered and washed with petroleum ether: 0.3 g; m p >220 °C. Anal. Calcd for C$_{14}$H$_{10}$S$_4$TiCl$_2$: C, 39.54; H, 2.37; S, 30.15; Ti, 11.26; Cl, 16.67. Found: C, 38.91; H, 2.55; S, 31.12; Ti, 11.51; Cl, 16.80.

Ti(dtb)$_4$. (a) The same procedure as for Ti(dtb)$_2$Cl$_2$ was used, starting from 8 mmol of dtbNa and 4 mmol of TiCl$_4$ in 15 mL of dichloromethane, yielding brown-red needles: 0.7 g; mp >220 °C. Anal. Calcd for C$_{28}$H$_{20}$S$_8$Ti: C, 50.89; H, 3.06; S, 38.81; Ti, 7.25. Found: C, 50.28; H, 3.02; S, 37.80; Ti, 8.01.

(b) Ti(dtb)$_4$ could not be synthesized, by the same procedure as above, by using ligand to metal ratios higher than 2. Within ~6 h, the reaction mixtures unavoidably consisted of a white-yellow solid and a violet solution. We were unable to obtain any well-defined solid from these solutions.

(c) The reaction between Ti(dtb)$_3$Cl (vide infra) and dtbNa afforded Ti(dtb)$_4$. A solution of Ti(dtb)$_3$Cl in dichloromethane (0.4 mmol in 50 mL) was added to a mixture of 4.5 mmol of dtbNa and 50 mL of dichloromethane. After the mixture stood ~36 h at room temperature, it was filtered and the product was isolated, with a ~10% yield, by reducing the volume of the filtrate to ~10 mL. The solid was washed with petroleum ether and diethyl ether.

Ti(dtb)$_3$Cl. Although this compound could not be prepared by reaction of TiCl$_4$ with dtbNa, it was the only well-defined species we could isolate by treating TiCl$_4$ with dtbH in a variety of experimental conditions and irrespective of the ligand to metal ratio.

(a) A 1.6-mmol portion of TiCl$_4$ was added to 16 mmol of pure dtbH, with stirring. The resulting dark red gummy mass was extracted with 100 mL of dichloromethane. After filtration, the volume of the filtrate was reduced to 20 mL. Upon cooling of the solution at -10 °C, bright red hexagonal plates were obtained: yield ~40%; mp 200-202 °C, dec. Anal. Calcd for C$_{21}$H$_{15}$S$_6$TiCl: C, 46.44; H, 2.79; S, 35.42; Ti, 8.82; Cl, 6.53. Found: C, 46.31; H, 2.74; S, 35.40; Ti, 9.12; Cl, 7.02.

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Table I. Infrared Frequencies (cm^{-1}) and Assignments of the Characteristic Absorptions of the Dithiobenzoato Complexes of Ti(IV) and V(V)

	ν(phen–C)	ν_{as}(CSS)	ν_s(CSS)	δ(CSS)	ν_{as}(MSS)	ν_s(MSS)	ν(Ti–Cl)
$Ti(dtb)_4$[a]	1250 vs	1009 s 999 s	931 s 928 sh	664 ms	370 sh	358 m	
$Ti(dtb)_3Cl$[a]	1257 vs	995 s	939 s 935 s	663 ms	375 vw	355 m	398 m[c]
$Ti(dtb)_2Cl_2$[a]	1247 vs	987 s 982 s	927 s	660 ms	360 sh	343 m	387 m
$VO(dtb)_3$[a]	1265 s 1245 w	1002 s 967 m	948 m 933 m	666 w 661 w	355 m	320 vw	
$VO(dtb)_3$[b]	1265 s 1245 w	1007 s 961 m	949 m 932 m	668 w 662 w			

[a] KBr pellets. [b] Carbon disulfide solution. [c] Tentative assignment.

(b) A ~0.8 M solution of $TiCl_4$ in dichloromethane was added dropwise to a ~0.9 M solution of dtbH in the same solvent. The addition was continued until no more $Ti(dtb)_3Cl$ separated, i.e., when the metal to ligand ratio was approximately 5.

Properties. $VO(dtb)_3$, $Ti(dtb)_2Cl_2$ and $Ti(dtb)_4$ can be handled in the air without visible decomposition. $Ti(dtb)_3Cl$ is stable in anhydrous conditions but releases HCl on exposure to air. All the solid complexes exhibit a small positive magnetic susceptibility (up to $\chi_{mol} = +400 \times 10^{-6}$ for $VO(dtb)_3$), which, as for other spin-paired dithio-[1,34] and perthiocarboxylates,[33] can be ascribed to the presence of ferromagnetic impurities. $VO(dtb)_3$ is slightly soluble (~5×10^{-3} M) in several organic solvents: acetonitrile, tetrahydrofuran, acetone, benzene, etc. The titanium derivatives are soluble (~10^{-2}–10^{-3} M) only in weakly polar or nonpolar media, in the order: $Ti(dtb)_4 \approx Ti(dtb)_2Cl_2 > Ti(dtb)_3Cl$. All solutions decompose rather rapidly, even when carefully dried and deoxygenated solvents are employed. Both freshly prepared and aged solutions (in tetrahydrofuran or acetone for $VO(dtb)_3$; in dichloromethane or nitromethane for the titanium complexes) showed a strictly nonelectrolytic behavior. Molecular weight measurements gave dilution- and time-dependent results which, however, never indicated the presence of polymeric species. Typical values for freshly prepared solutions are as follows: $VO(dtb)_3$, 510 in tetrahydrofuran (0.29%) and 400 in acetone (0.25%) (calcd 527); $Ti(dtb)_3Cl$, 460 in toluene (0.20%) (calcd 543).

Measurements. These were performed as described previously.[1]

Results and Discussion

$Ti(dtb)_nCl_{4-n}$ (n = 2, 3, or 4) and $VO(dtb)_3$ are nonelectrolytic, diamagnetic species and a monomeric nature is the most likely for all of them.

A main purpose of the present work was to establish the detailed geometry of potentially seven- or eight-coordinate complexes by X-ray methods. Unfortunately, the many attempts to obtain single crystals of $Ti(dtb)_4$ and $VO(dtb)_3$, in any considerable size, failed completely. No better results were obtained from the corresponding compounds with the p-$CH_3OC_6H_4CSS^-$ ligand, which were prepared in an attempt at modifying the crystallization forces without appreciably affecting the overall electronic energy. $Ti(dtb)_3Cl$ gave single crystals of suitable size, but they decomposed under the X radiation. In the absence of X-ray data the coordination numbers were inferred from the vibrational spectra. Selected frequencies are reported in Table I. They have been assigned following previous lines of discussion.[35-37] The remaining absorptions are associated with the aromatic group and can be identified completely as their frequencies and intensities agree with those usually observed for light and heavy monosubstituted benzenes. The antisymmetrical and symmetrical carbon–sulfur stretching frequencies (and their separation) are intermediate between those of crystalline dtbNa (1018 and 925, 916 cm^{-1})[35] and those (~1015 and ~945 cm^{-1}) of $Mo(dtb)_4$,[1] $V(dtb)_4$,[17,25] or $Ni(dtb)_2$,[35,37] which are known to be completely chelated. Different frequencies[35] (ν_{as} 1065 and ν_s 841 cm^{-1}) are shown by, e.g., dtbH, in which the dithiocarboxylic group is asymmetrical because of the covalent S–H bond. It can also be noted that ν_{as}, ν_s, and ν(phen–C) of $Ti(dtb)_4$ are all shifted in the same direction with respect to the corresponding frequencies of $Mo(dtb)_4$ and $V(dtb)_4$, indicating that the bond orders of both the C–S bonds in the approximately symmetrical CS_2 groups in the latter compounds are changed by the same amount. Bands attributable to monodentate dtb ligands, logically expected at frequencies ≥1065 and ≤841 cm^{-1}, were not observed. The spectra, therefore, are indicative of only bidentate dtb attachment and coordination numbers of 6, 7, and 8 for the $M(dtb)_nX_{4-n}$ species, when n = 2, 3, and 4, respectively. The same conclusion is suggested by the known structures of the corresponding dithiocarbamates.[13,27,30]

Why each complex exhibits more than two carbon–sulfur stretching bands is not understood. The case of $VO(dtb)_3$ is the most noteworthy since the presence of four distinct bands in the C=S stretching region (which, however, should also contain the V–O stretching) is paralleled by the doubling of the ν(phen–C) and δ(CSS) frequencies. This behavior is unlikely to arise from intermolecular interactions: bands with the same relative intensity and position are present in carbon disulfide. Inequivalence of the chelating ligands, according to, e.g., a pentagonal-bipyramidal structure,[38] with the axial ligand somewhat distorted with respect to the equatorial ones could provide an alternative explanation of the multiplicity of the bands. In this regard, it is of interest that $NbO(S_2CNEt_2)_3$ and $VO(S_2CNEt_2)_3$ parallel the spectral behavior of $VO(dtb)_3$ (30 cm^{-1} splitting of the C=N band and more than one band in the C=S region[28,29]) and actually adopt a pentagonal-bipyramidal configuration with the oxygen atom at an axial site.[30] Whether this might imply a similar structure for $VO(dtb)_3$ remains uncertain. Significant differences in bond lengths or angles between the dithiocarbamato ligands are not discernible from the X-ray structures.[30] Further, $Ti(S_2CNMe_2)_3Cl$, also pentagonal bipyramidal,[27] has the axial bidentate ligand clearly distorted with respect to the other ones but does not exhibit any splitting of the C=N band and shows only a closely spaced doublet (separation 9 cm^{-1}) in the C=S region.[26] It appears, therefore, that stereochemical predictions made through an empirical use of group frequencies are likely to be misleading when applied to molecules of the type considered here, even making allowance for the fact that differences in C–S and C–N bond lengths might be masked by the inaccuracy of the structural parameters. The region between 300 and 400 cm^{-1} contains the metal–sulfur and titanium–chlorine stretching frequencies. The bands at 398 and 387 cm^{-1} in the mono- and dichlorotitanium complexes, respectively, have been assigned to ν(Ti–Cl) since they have no counterpart in $Ti(dtb)_4$ or $VO(dtb)_3$. However, a ν(Ti–Cl) frequency of 398 cm^{-1} in $Ti(dtb)_3Cl$ is anomalous. The expected frequency[41] is ~350–370 cm^{-1}. Possibly, ν(Ti–Cl) is responsible, at least in part, for the band at 355 cm^{-1}, and the band at 398 cm^{-1} has a different origin.

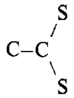
The ν(V–O) stretching mode in $VO(dtb)_3$ cannot be located with certainty, due to the occurrence of the C=S bands in the region in which it is usually observed (950–1100 cm^{-1}).[41]

Table II. Electronic Spectra of the Ti(IV) and V(V) Dithiobenzoato Complexes and Related Systems[a,b]

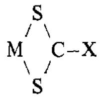
	medium	band I	band II	bands III		ref
dtb^-	H_2O	20.8 (2.15)		28.2 (3.70)	34.1 (3.63)	*c*
$Ti(dtb)_2Cl_2$	Nujol	18.3		30.8	33.0	this work
$Ti(dtb)_3Cl$	Nujol	18.2	19.4	26.8	33.3	this work
$Ti(dtb)_4$	Nujol	16.5 sh	23.1	30.8	32.6	this work
$VO(dtb)_3$	Nujol	19 sh	24.7	29.8	33.3	this work
$Zn(dtb)_2$	$CHCl_3$	21.0 (1.50)		27.2 (4.03), 30.4 (4.56)		*c*
$Pb(dtb)_2$	C_6H_6	21.3 (2.91)		26.4 (3.99), 30.9 (4.70)	34.1 (4.46)	*d*
$In(dtb)_3$	$CHCl_3$	22.4 (3.20)		26.0 (4.09), 30.9 (4.83)	33 sh (4.59)	*d*
$Et_2NCS_2^-$	H_2O	28.6 (1.74)		34.6 (4.11), 38.9 (4.1)		*e*
$Ti(S_2CNEt_2)_4$	CH_2Cl_2		25.0 sh (4.78)	35.7 (4.79), 42.6 sh (4.65)		*f*
	reflect	29.2	25.3	36.9		*g*

[a] Absorption maxima are reported in $cm^{-1} \times 10^3$; sh = shoulder; log ϵ in parentheses. [b] The solution spectra of the Ti(IV) and V(V) dtb complexes were not reliable; only solid-state spectra are reported. [c] Reference 34. [d] Reference 45. [e] C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962). [f] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969). [g] Reference 28.

Electronic Spectra. The electronic absorption spectra of the present complexes, together with those of some related species, for purpose of comparison, are reported in Table II. According to simple MO theory[42] and to the results of a recent photoelectron spectroscopy investigation[43] of several dithio derivatives of the carboxylate group, the highest occupied molecular orbitals of a planar

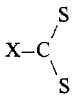


chromophore (C_{2v} symmetry) can be described, in order of decreasing energy, as follows. (i) ψ_n (B_2 symmetry), the antisymmetric combination of the in-plane lone-pair p_y orbitals of the sulfur atoms, is perpendicular to the adjacent C–S lines. (ii) π_2 (A_2 symmetry), a molecular orbital localized on the sulfur atoms, is built up by the out of phase overlap of a p_z orbital on each sulfur atom. (iii) Next are located the highest energy σ-bonding orbital (delocalized on the four atoms) and a π-bonding molecular orbital (B_1 symmetry) having the p_z orbital of the central carbon atom overlapping in phase with the p_z orbitals of the sulfur atoms and out of phase with the p_z of the terminal carbon atom. The lowest vacant MO is π_3 (B_1 symmetry), an antibonding orbital having the p_z orbital of the central carbon atom overlapping out of phase with each of the p_z orbitals on the sulfur atoms and in phase with the p_z orbital of the terminal carbon atom. It is assumed, as a first approximation, that the lone-pair s orbitals of sulfur remain essentially atomic in character, as suggested by the known structures of transition-metal dtb and dtc complexes with coordination numbers 7 or 8, in which the



units are essentially planar with M–S–C angles close to 90°.

In the free ligand the lowest energy $\pi \rightarrow \pi^*$ transition, from π_2 to π_3, gives rise to a moderately strong band at 28 200 cm^{-1} and the transition from ψ_n to π_3 (symmetry forbidden) to the weak $n \rightarrow \pi^*$ band at 20 800 cm^{-1}. Both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are shifted approximately 7000 cm^{-1} to higher energy in $R_2NCS_2^-$, irrespective of the nature of the R substituent. This effect is in agreement with the notion that ψ_n and π_2 are essentially localized on the sulfur atoms and nonbonding to the rest of the



system (therefore with energy little dependent on the rest of the molecule), while π_3 is delocalized over the whole system, with an energy which is expected to increase[44] when a phenyl group is substituted by a R_2N group, a much better donor.

The spectra of the $Ti(dtb)_nCl_{4-n}$ and $VO(dtb)_3$ species are fairly similar. A band of very low intensity (except for $Ti(dtb)_2Cl_2$) occurs between ~16 000 and ~19 000 cm^{-1} (band I), followed by the moderately intense band II (19 000–25 000 cm^{-1}). Above 29 000 cm^{-1} (except for $Ti(dtb)_3Cl$, which shows a strong absorption at ~27 000 cm^{-1}) occur bands III, of the highest intensity. Perturbed dtb transitions of mainly $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ character are the most likely origin of bands I and III, respectively. Similar bands are exhibited by the free ligand[34] and by other dtb complexes of closed-shell configuration.[34,45]

Bands II have no counterpart either in the spectra of the free ligands or in those of dtb complexes of nonreducible metal ions such as Zn(II). Therefore, they may be attributed mainly to a transfer of charge to the metal, and the optical electronegativity values of dtb (2.6),[45] Cl^- (3.0),[46] and O^{2-} (3.2)[46] (in cubic microsymmetry) leave little doubt that the donor ligand is dtb in each complex. In $Ti(dtb)_2Cl_2$, the band at 18 300 cm^{-1} has high intensity and probably encompasses both the $n \rightarrow \pi^*$ and the charge-transfer transitions.

A spectral feature of the d^0 dtb complexes, which has significant implications to the understanding of the hitherto unexplained profound differences between the spectra of dtb[1,25] and dtc[24,28] eight-coordinate complexes of d^1 and d^2 metal ions, is the energy of the $n \rightarrow \pi^*$ transition and its position relative to the first charge-transfer band.

Unlike d^{10} or s^2 dtb complexes[34,45] (and $Ti(S_2CNEt_2)_4$ as well) which show the $n \rightarrow \pi^*$ band either unaltered or slightly blue shifted with respect to the free ligand, the d^0 complexes exhibit a definite red shift, up to ~4000 cm^{-1} in $Ti(dtb)_4$. This indicates an excess of stabilization in the upper state over that in the ground state, upon complex formation, which is rather unusual since the n electrons are σ bonding to the metal.

A tentative explanation of these effects is according to the previous MO description. In free dtb (and dtc as well) ψ_n has very little charge on the carbon atoms. In π_3 charge is more evenly distributed between the p_z orbitals of the $C–CSS^-$ chromophore, so the lowest energy absorption results in a net transfer of electron density from sulfur to carbon, or, better, to the whole π system, including the phenyl ring. When the ligand is coordinated to the d^0 metal, some of the negative charge of the π system in the upper state might migrate into the metal, thus stabilizing the excited state and lowering the energy of the transition. Such a delocalization of π-electron density is unlikely for either d^{10} or s^2 complexes, and, as judged by the relative energies of band I in $Et_2NCS_2^-$ (28 600 cm^{-1}), $Ti(S_2CNEt_2)_4$ (29 200 cm^{-1}),[28] and in other dtc complexes with closed-shell configuration,[47] it is less effective for the d^0 dithiocarbamates. It might be argued that the high energy of

π_3 in dtc is responsible for this behavior, by allowing a less efficient mixing with the metal d orbitals. The spectra of the d^0 species seem to indicate, therefore, that the dtb ligand system has vacant antibonding orbitals at more suitable energy to interact with the d metal functions than the dtc ligand system. If so, the d–d states in a d^1 or d^2 dtb complex will be much less well defined than in the corresponding dithiocarbamates. The much higher intensity of the low energy transitions in $V(dtb)_4$, $Mo(dtb)_4$ than in $V(dtc)_4$, $Mo(dtc)_4$ is clearly in agreement with this conclusion.

Concluding Remarks. The formation and properties of the $Ti(dtb)_nCl_{4-n}$ and $VO(dtb)_3$ species seem to reinforce the view that metal–ligand π interactions mainly involving the low-lying π^* orbitals of dtb have a definite role in the stability and stereochemistry of eight-coordinate transition-metal dtb complexes. Only eight-coordinate, dodecahedral species are formed by Mo(IV) and V(IV) with dtb, irrespective of the metal to ligand ratio and reaction conditions, while, in the case of Ti(IV), six-, seven-, and eight-coordinate compounds are obtained. On the whole, the latter seem to be the result of simply picking the right combination of reactants, the right reaction medium, or the right reaction conditions. It must be admitted that all of the $Ti(dtb)_nCl_{4-n}$ complexes exhibit a larger degree of thermodynamic instability than $Mo(dtb)_4$ or $V(dtb)_4$. Even the chemical stabilities in solution are in the order Mo(IV) > V(IV) > Ti(IV).

These observations are compatible with the expectation that the relative importance of the d π^* interactions should decrease in the order $d^2 > d^1 > d^0$.

A last remark concerns corresponding dtb and dtc complexes. The marked differences between their properties are very unlikely determined by steric or σ-bonding effects and seem to be rather due to π-interactions of a different type. As described above, π_3 is at higher energy in dtc than in dtb. Apparently this results in a greatly reduced π-acceptor character of the former ligand and in an increased contribution of its filled π orbitals to the bonding with the metal. This may be exemplified by the different effects that dtb and dtc exert on the vanadium–oxygen multiple bond of the VO^{2+} oxocation. dtc forms[48,49] $VO(dtc)_2$ species (C_{2v} symmetry[50]) having an increasing oxygen to vanadium axial bonding with decreasing sulfur to metal π bonding, i.e., decreasing donor character of the substituents. dtb, with a much weaker donor linked to the $-CS_2^-$ group, destroys the vanadium–oxygen multiple bond to produce $V(dtb)_4$.[25] The fact that the multiple bond is maintained in $VO(dtb)_3$ points to the relevance of the d-electron delocalization in stabilizing the nonoxocation species. Thus, other things being equal, dtc is expected to interact more favorably (via π bonding) than dtb with a d^0 system and less favorably with a d^2 system. The dodecahedral symmetry of $Ti(S_2CNEt_2)_4$ and its greater thermodynamic stability with regard to six-and seven-coordinate species (these compounds are formed simply by using[26] stoichiometric ligand to metal ratios) agree with this view, as do the dodecahedral symmetry of $Mo(dtb)_4$, the distorted antiprismatic geometry (allowing much less effective π interactions) of $Mo(S_2CNEt_2)_4$, and the variations of the spectroscopic and polarographic properties.

Registry No. $Ti(dtb)_4$, 70178-71-1; $Ti(dtb)_3Cl$, 70178-72-2; $Ti(dtb)_2Cl_2$, 70178-73-3; $VO(dtb)_3$, 70178-74-4; $VOCl_3$, 7727-18-6; $VOCl_2$, 10213-09-9; $Zn(C_6H_5CS_2S)_2$, 30210-13-0; $TiCl_4$, 7550-45-0; VCl_3, 7718-98-1; $V(dtb)_4$, 31871-44-0.

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