The complexes were prepared according to standard procedures. In general the ligand (0.002 mol for ligands except DP, PN, and PDN which were used in 0.001-mol quantities) was added dropwise in dry benzene or methylene chloride (*ca.* 10 ml) to a solution of the tin tetrahalide (0.001 mol) in the same solvent (*ca.* 10 ml). In most cases the complex separated immediately or soon after mixing. Complex I separated as an oil which crystallized slowly beneath petroleum ether (bp 40–60°). Complex X could not be prepared in methylene chloride since rapid exchange took place in this solvent to precipitate complex IX. Complexes XXIV and XXV are freely miscible in petroleum ether and could not be recrystallized. The DMSO complexes VII and VIII were prepared by the general method of Cotton, *et al.*[39]

The complexes are usually white powders or microcrystalline solids (from $SnCl_4$) or colored crystalline solids (from $SnBr_4$ and $SnI_4$) and were characterized by melting point and published infrared spectra if known. New compounds, which are starred in Table I, were characterized by melting point and infrared spectral comparisons with similar, published complexes. Microanalytical data for C, H, and Sn were recorded only for key examples of these parallel series and are listed in Table I.

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# Eight-Coordination. I. Dodecahedral Vanadium(IV) Complexes with Sulfur-Chelating Ligands

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Dithiocarboxylates (L = $C_6H_5$–$CSS^-$ = $dtb^-$, *p*-$CH_3$–$C_6H_4$–$CSS^-$ = $dtt^-$, $CH_3$–$CSS^-$ = $dta^-$, $C_6H_5$–$CH_2$–$CSS^-$ = $dtpa^-$) react with both $VO^{2+}$ ion and V(III) to give stable $VL_4$ complexes. Magnetic measurements, infrared spectra, and molecular weight measurements in solution are consistent with eight-coordinated V(IV). Epr and preliminary X-ray results demonstrate an approximate $D_{2d}$ geometry for the $VS_8$ chromophores. Electronic spectra are discussed.

## Introduction

Increasing interest is being shown in the chemistry of complexes involving second-row donor atoms, especially sulfur. A main stimulus is the rationalization of the increasing number of unusual steric and electronic properties of these complexes, on the basis of specific differences in polarizability, covalency, $\pi$-bonding ability, etc., between second- and first-row donor atoms.

Related to these studies are recent preparations and characterizations of some V(IV) complexes with sulfur-chelating ligands. Direct reaction of $VO^{2+}$ ion with $R_2NCS_2^-$ in water gives "normal" $VO(R_2NCS_2)_2$ complexes[1,2] for which the usual $C_{4v}$ symmetry has been suggested. Eight-coordinate $V(R_2NCS_2)_4$ complexes are obtained[3–6] from insertion reactions of $CS_2$ and $V(NR_2)_4$ in dry cyclohexane, under dry, oxygen-free conditions. Apart from some "noninnocent" 1,2-dithiolenes[7,8] and $S_2P(OEt)_2^-$ (which produces V(III),[9] the behavior toward $VO^{2+}$ of no other system of this type has been characterized, in contrast to the hundreds of $VO^{2+}$ complexes with N, O, or Cl donor ligands which have been studied in detail.[10]

In this paper an extension of the coordination chemistry of dithiocarboxylates to V(IV) is described. The main result is the cleavage of the oxo–vanadium bond by R–$CSS^-$ ions with the consequent formation of V(R–CSS)$_4$ species for which an eight-coordinate, dodecahedral structure is established. A preliminary interpretation of the electronic structure is also given.

## Experimental Section

**$VCl_3$, $VOSO_4 \cdot 2H_2O$, $VOCl_2 \cdot nH_2O$, $VCl_4$.**—These compounds were obtained commercially and were used as received.

**Ligands.**—Acids and sodium salts were prepared following known procedures: $C_6H_5$–CSSH(dtbH),[11] *p*-$CH_3$–$C_6H_4$–CSSH (dttH),[12] $CH_3$–CSSH (dtaH),[13] $C_6H_5$–$CH_2$–CSSH (dtpaH).[14]

**Complexes.**—The vanadium(IV) complexes with the above dithiocarboxylates may be obtained very easily as impure products. Addition of an aqueous solution of vanadyl chloride or sulfate to aqueous solutions of the sodium salts of the ligands causes immediate precipitation of dark yellow, gummy masses. Little, if any, difference may be noted among the behavior of the different ligands. Powders were obtained, on washing and drying these products, which gave chemical analyses roughly in agreement with a stoichiometry $V(RCSS)_4$.

Powders with approximately the same elemental analyses and melting points can be obtained by adding the ligands, as free acids, dissolved in the minimum amount of ether, to an alcoholic solution of vanadyl sulfate or chloride.

Replacement of vanadyl salts by vanadium trichloride leads to similar products in both water and alcohol.

In spite of their simplicity, the two methods described are not suitable since attempts to purify the crude products by recrystallization from inert solvents, chromatography, etc., were unsuccessful. Decomposition occurred in all cases. To avoid this difficulty, a procedure had to be found which gave pure reaction products directly, for reliable and reproducible chemical and physical measurements. The following methods were the most successful.

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Table I

Elemental Analyses

| Compd | % C Calcd | % C Found | % H Calcd | % H Found | % S Calcd | % S Found | % V Calcd | % V Found |
|---|---|---|---|---|---|---|---|---|
| V(dta)$_4$ | 23.12 | 23.20 | 2.92 | 2.88 | 61.71 | 61.90 | 12.26 | 11.94 |
| V(dtb)$_4$ | 50.65 | 50.27 | 3.04 | 3.02 | 38.63 | 39.18 | 7.67 | 7.63 |
| V(dtpa)$_4$ | 53.38 | 53.22 | 3.93 | 3.98 | 35.62 | 34.39 | 7.07 | 6.51 |
| V(dtt)$_4$ | 53.38 | 53.56 | 3.93 | 4.08 | 35.62 | 36.04 | 7.07 | 6.90 |

**V(dtb)$_4$.**—To a variable, but known, volume of ~0.03 *M* solution of vanadyl chloride or vanadium trichloride in absolute ethanol was added an equal volume of a ~0.3 *M* solution of the dithiocarboxylic acid in ether. The addition was made dropwise over a period of ~40 min, with stirring. Nitrogen was bubbled through the reaction mixture and additional ether was added when it occasionally became turbid. In the final reaction mixture, ether was in the minimum amount to have a clear solution. Gradual crystallization was then achieved on slow evaporation at room temperature. The first bright, dark red, transparent crystals were obtained after several hours, mp 137°. Progressive fractions of crystals were collected. The last ones had melting points progressively lower than the first and were discarded, since no suitable solvent was found to recrystallize them without decomposition. The yield of final product with mp 137° was ~15%, referred to original vanadium.

Different preparations gave quite reproducible elemental analyses, melting points, etc.

**V(dtpa)$_4$, V(dta)$_4$.**—The same procedure as for V(dtb)$_4$ was used to obtain these pure compounds. The first red, triclinic crystals of V(dtpa)$_4$ formed in about 24 hr, mp 84°, yield ~25%. V(dta)$_4$ required 2–3 days to give dark-red, prismatic crystals, mp 115°, yield ~8%.

**V(dtt)$_4$.**—The compound can be isolated as above, mp 132°, yield ~30%. Only microcrystalline powders were obtained in this case since even a large excess of ether in the reaction mixture could not prevent fast precipitation. Well-formed, red crystals were obtained by adding a carbon disulfide solution of Zn(dtt)$_2$[15] to an absolute ethanol solution of vanadium trichloride and cooling the reaction mixture at 0° for ~24 hr.

Analytical data for the four new complexes are in Table I.

Infrared and electronic spectra of the crystalline substances were similar to those of the crude products obtained from water or alcohol, so V(R–CSS)$_4$ has to be a main component of those powders.

The four complexes are similar in their properties. When pure, they are not air-sensitive and can be kept unaltered for long periods. They are insoluble in polar solvents, and generally soluble in nonpolar ones. However, the solutions decompose rapidly and physical measurements were performed on them immediately after preparation.

**Chemical Analyses.**—Complex formation between VO$^{2+}$ and EDTA was used for the determination of vanadium. Water-soluble materials were obtained from the complexes after fusion with a 50% mixture of $Na_2O_2$ and $Na_2CO_3$. Fuming $HNO_3$ or 70% $HClO_4$ were ineffective. After reduction to V(IV) by sodium sulfite at pH ~5 a small excess of EDTA was added and the resulting solution was titrated with $ZnCl_2$, using standard procedures.[16] Xylenol Orange was used as indicator.

Treatment with an $H_2SO_4$–$HNO_3$ mixture, followed by reduction with zinc amalgam and titration with $KMnO_4$,[17] gave nonreproducible results, probably because of interference by the organic decomposition products formed.

C, H, and S analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, the Scandinavian Mikroanalytical Laboratory, Herlev, Denmark, and Laboratorio di Microanalisi, Padua, Italy. These laboratories reported that high-temperature combustion was necessary because of the formation of very temperature-stable decomposition products.

**Magnetic Moments.**—Magnetic susceptibilities were measured on solid polycrystalline samples by the Gouy method, between ~90 and ~300°K and at several field strengths to check for anti- and ferromagnetism. Pascal's constants were used to correct the measurements for diamagnetism of the cation and the ligands. For V(dta)$_4$, measurements were repeated by the Faraday method to correct for ferromagnetic impurities.[18]

**Molecular Weights.**—Molecular weight measurements were performed with a Mechrolab Model 301A vapor pressure osmometer. Freshly prepared solutions in $C_2H_4Cl_2$ or $C_6H_6$ were used, since decomposition with time occurs in these and in any other solvent. V(dtpa)$_4$: found, 610; calcd, 720; V(dta)$_4$: found, 340; calcd, 416; V(dtb)$_4$: found, 702; calcd, 664; V(dtt)$_4$: found, 698; calcd, 720.

**Infrared Spectra.**—These were measured on Nujol and Fluorolube mulls on Beckman IR 10 and Perkin Elmer 521 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. The investigated ranges of concentrations for the solutions were $10^{-2}$–$10^{-3}$ *M* for the visible and $10^{-3}$–$10^{-5}$ *M* for the ultraviolet region.

Single-crystal spectra (350–800 mμ) were measured on a Shimadzu MPS 50L spectrophotometer.

**Epr Spectra.**—These were recorded on a Varian V 4502-12 A operated at X-band frequencies.

## Results and Discussion

**(A) Stoichiometry and Stereochemistry.**—In this section we describe how analytical data, magnetic measurements, and spectroscopic methods were first used to establish the stoichiometry and stereochemistry of the V(R–CSS)$_4$ complexes. Later, two collateral X-ray determinations became available and the agreement between the two sets of results is discussed.

Analytical data for the new compounds are reported in Table I. Magnetic measurements confirmed the presence of a d$^1$ system.

**Magnetic Moments.**—For V(dtpa)$_4$, susceptibility measurements show Curie–Weiss behavior with $\Theta = -20°$ suggesting magnetic interaction in the solid. However, the corrected value of $\mu_{eff}$ was constant over the whole temperature range (1.70 ± 0.02 BM) and agreed with that (1.71 BM) calculated from the $\bar{g}$ value (1.978) (*vide infra*). V(dta)$_4$ shows the same behavior in the range 77–200°K ($\mu_{eff} = 1.72 \pm 0.02$, $\Theta = -20°$), but between 200 and 293°K $\mu_{eff}$ was found to increase with temperature up to 1.87 BM at 293°K. The presence of ferromagnetic impurities, undetectable by chemical analyses, seems to be the most probable origin of this phenomenon, since the Faraday method gave a $\mu_{eff}^{293}$ of 1.74 BM.

For V(dtb)$_4$ and V(dtt)$_4$ the Curie–Weiss law was not obeyed and $\mu_{eff}$ values were between 1.70–1.79 and 1.68–1.75 BM, respectively, in the range 92–295°K. These magnetic moments do not show any simple correlation with *T*°K, particularly that expected from the presence of orbital angular momentum in the ground state.[19] Again the presence of impurities seems to be the most probable origin of the observed magnetic interactions.

On the whole, although the present experimental material in some case does not allow a detailed interpretation, little doubt is left about a +4 oxidation state

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TABLE II[a]

INFRARED SPECTRA (CM$^{-1}$) OF $VL_4$ COMPLEXES BETWEEN 400 AND 1300 CM$^{-1}$

| $V(dta)_4$ | Assignment | $V(dtpa)_4$ | $V(dtb)_4$ | $V(dtt)_4$ | Assignment |
|---|---|---|---|---|---|
| 447 w | $\omega$(CSS) | 450 vw | 437 w | 453 w | $\pi$(phenyl ring) |
| | | 470 m | | | |
| 540 vw | Comb. | 575 m | 569 vw | 563 vw | Phenyl and $-CH_3$ |
| | | | | 592 w | |
| 600 w, br | Not assigned | 615 vw | 613 vw | 630 vw | $\alpha$(C–C–C) |
| 725 w | Comb. | 645 m | 668 w | | $\delta$(CSS) |
| | | 655 sh | | | |
| 860 s | $\bar{\nu}_s$(CSS) | 690 s | 678 s | 790 m | $\pi$(C–H) mono- or disubstituted benzene ring |
| | | 752 s | 760 s | 820 s | |
| 1020 w | Comb. | 798 w | 802 vw | | $\pi$(C–H) |
| | | 810 w | 840 vw | | $\omega$x |
| 1100 sh | $\rho(CH_3)$ | 840 m | | | Not assigned |
| | | 850 sh | | | |
| 1147 s | $\bar{\nu}_{as}$(CSS) | 903 w | 930 sh | | |
| 1173 s | | | 945 ms | 948 s | $\bar{\nu}_s$(CSS) |
| 1270 w | Comb. | 960 sh | 980 sh | 982 w | Not assigned |
| 1357 m | $\delta_s(CH_3)$ | 1000 sh | | | |
| | | 1010 sh | 1000 w | 1000 sh | Ring breathing |
| | | | | 1020 sh | |
| | | 1020 vs[b] | 1015 s | 1031 s | $\bar{\nu}_{as}$(CSS) |
| | | 1072 s | | | $\bar{\nu}(CH_2)$ |
| | | 1127 vs | | | $\bar{\nu}_{as}$(CSS)? |
| | | 1150 sh | 1160 sh | 1128 vw | Not assigned |
| | | 1180 w | 1180 m | 1180 vs | $\rho$(C–H) |
| | | 1200 w | 1210 sh | 1240 sh | $\omega$x and $\delta$(C–H) |
| | | | 1230 sh | | |
| | | 1290 w? | 1260 vs | 1262 vs | $\bar{\nu}$(phenyl–C) |
| | | 1335 w | 1320 w | 1315 w | $\bar{\nu}(C–C)_{phenyl}$ |

[a] Abbreviations: $\pi$, out-of-plane bending; $\rho$, in-plane bending; $\delta$, deformation; $\bar{\nu}$, stretching; $\omega$x, substituent-sensitive phenyl vibrations; $\omega$, wagging; comb., combination. [b] Possibly $\bar{\nu}_s$(CSS).

for the vanadium atom. This conclusion is further supported by the epr measurements (*vide infra*).

The reactivity of the dithiocarboxylates toward $VO^{2+}$ or V(III) to produce air-stable $V(RCSS)_4$ in strongly oxygenated solvents involves at least three different features which are unusual for both the metal and the ligands.

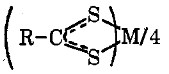
(a) Since the oxidation state of vanadium is preserved in the reactions involving $VO^{2+}$ ion, one step must necessarily be the cleavage of the vanadium–oxygen multiple bond.

Since this bond is commonly described using the $d_{z^2}$*, $d_{xz}$*, and $d_{yz}$* antibonding orbitals of the metal ion, a transition state is suggested in which an unusually strong interaction between these orbitals and the ligand $\pi$-orbital system exists.

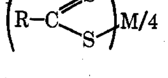
(b) Oxidation of V(III) to produce $VL_4$ complexes contrasts with the general reducing character of sulfur-containing ligands and indicates stabilization of the +4 oxidation state of the vanadium atom in complexes of this type.

(c) The presence of an uncommon $VS_8$ chromophore is suggested in these complexes.

**Infrared Spectra and Molecular Weights.**—For eight-coordination to be achieved, a common structure



is required in the $VL_4$ unit. Obviously, a coordination number of 4 could also be attained, *e.g.*, as in



and the intermediate cases are a third possibility. Since differently conjugated bonds in the CSS groups should give $\bar{\nu}$(CSS) stretching modes at different frequencies, ir spectra have been used to distinguish between different cases.

Infrared frequencies for the $VL_4$ complexes are in Table II; in Table III selected frequencies for other dithiocarboxylato compounds are reported for comparison.

The assignments in Table II have been made by comparison with the spectra of the free ligands,[20–22] the corresponding carboxymethyl dithio esters,[23] and square-planar $NiL_2$ complexes[21,22] (involving the same ligands as the $VL_4$ complexes) in which a bidentate structure for the ligands has been proved by spectroscopic and X-ray methods.[24–26]

A strong band in the vicinity of 1225 cm$^{-1}$ and a medium-intensity band at about 670 cm$^{-1}$ have been identified by Bak, *et al.*,[23] as $\bar{\nu}$(C=S) and $\bar{\nu}$(C-S), respectively, for the dithio esters. These assignments have been confirmed by Bellamy and Rogasch[27] *via* solvent studies.

In aliphatic dithio acids $\bar{\nu}$(C=S) and $\bar{\nu}$(C—S) are little shifted from the former values while in aromatic dithio acids these frequencies are found at lower and higher energies, respectively.[21] If a monodentate ligand were present in $VL_4$ complexes, similar bands at approximately the same frequencies as $\bar{\nu}$(C=S) and $\bar{\nu}$(C—S) of the corresponding dithio esters or dithio acids would be expected. In no case were bands attrib-

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TABLE III

$\bar{\nu}_s$(CSS) AND $\bar{\nu}_{as}$(CSS) FREQUENCIES (CM$^{-1}$) FOR DIFFERENT DITHIOCARBOXYLATO COMPOUNDS

| | dtaR[a] | dtaH | V(dta)$_4$ | dtpVH | Ni(dtpV)$_2$ | dtpaR[a] | dtpaH | V(dtpa)$_4$ | Ni$_2$(dtpa)$_4$ |
|---|---|---|---|---|---|---|---|---|---|
| $\bar{\nu}_s$(CSS) | 668 | 581 | 860 | 778 | 953 | 663 | 670 | 1020? | ? |
| $\bar{\nu}_{as}$(CSS) | 1225 | 1192[b]<br>1216 | 1147<br>1173 | 1220 | 1048 | 1215 | 1225 | 1127? | 1041? |
| Ref | 22 | 20 | c | 21 | 21 | 23 | 21 | c | 21 |

| | dtbR[a] | dtbH | dtbNa | V(dtb)$_4$ | Ni(dtb)$_2$ | dttR[a] | V(dtt)$_4$ | Ni(dtt)$_2$ |
|---|---|---|---|---|---|---|---|---|
| $\bar{\nu}_s$(CSS) | 667 | 841 | 910 | 945 | 945 | 666 | 948 | 948 |
| $\bar{\nu}_{as}$(CSS) | 1226 | 1065 | 1018 | 1015 | 980 | 1225 | 1031 | 972 |
| Ref | 23 | 22 | 22 | c | 22 | 21 | c | 21 |

[a] R = carboxymethyl group. [b] Found at 1190–1210 in $CD_3CSSH$ (this work). [c] This work; dtpV$^-$ = $(CH_3)_3C$–$CSS^-$; dtpVH = $(CH_3)_3C$–CSSH.

TABLE IV

EPR PARAMETERS[a] OF V(IV) DITHIOCARBOXYLATES

| | $g_\perp$ | $g_\parallel$ | $g_{av}$ |
|---|---|---|---|
| V(dta)$_4$ | 1.977 | 1.969 | 1.974 |
| V(dtpa)$_4$ | ... | ... | 1.978[b] |
| V(dtb)$_4$ | 1.981 | 1.962 | 1.975 |
| V(dtt)$_4$ | 1.981 | 1.966 | 1.976 |

[a] From room-temperature powder spectra. [b] Approximate value, broad signal.

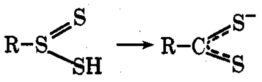
TABLE V

ELECTRONIC SPECTRA OF THE L$^-$ LIGANDS AND THEIR V(IV) COMPLEXES[a]

| | | Tentative assignments | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compd | Medium | Mainly ligand field transitions | | | | | | | n → $\pi^*$(C=S) | CT | Ligands $\pi \rightarrow \pi^*$ plus possible CT | |
| dtaNa | $H_2O$ | | | | | | | | 22.4 (1.62) | | | 30.0 (4.19) |
| dtaH | $(C_2H_5)_2O$ | | | | | | | | 19.6 (1.26) | | | 34.1 (4.06) |
| V(dta)$_4$ | $CH_2Cl_2$ | 12.8 sh (1.78)[b] | | | | | | 19.2 sh (2.50) | | 21.7 sh (3.76) | | 33.1 (4.15) |
| | $CH_2Cl$–$CH_2Cl$ | 13.1 sh | | | | | | 18.8 sh | | 22.2 sh | | 32.8 (4.20) |
| | Nujol[c] | 11.8[d] | | | | | | 19.2 sh | | | | 33.3 |
| | e | 12.8 sh | 13.4 | 15.3 | 16.4 sh | 17.1 | 18.2 sh | 19.2 sh | | 22.9 | | f |
| dtpaNa | $H_2O$ | | | | | | | | 20.8 (1.65) | | | 29.4 (3.90) |
| dtpaH | $(C_2H_5)_2O$ | | | | | | | | 20.8 (1.36) | | | 34.1 (3.74) |
| V(dtpa)$_4$ | $CH_2Cl_2$ | 12.4 sh (1.61) | | | 13.3 sh (0.71) | | | 18.9 sh (2.46) | | 21.3 sh (3.14) | 27.0 sh (3.52) | 34.1 (4.34) |
| | $C_6H_6$ | 12.5 sh | | | 13.7 sh (1.80) | | | 18.8 sh (2.83) | | 23.8 sh (3.55) | | f |
| | $CH_2Cl$–$CH_2Cl$ | 12.4 sh | | | 13.7 sh | | | 19.2 sh | | 23.8 sh | | f |
| | Nujol[c] | 12.5 | | | | | | 18.8 sh | | 21.7 sh | 26.4 sh | 32.0 |
| | Nujol (77°K) | 12.1 | | | 13.4 sh | | | 18.5 sh | | 21.3 | 26.3 sh | 31.4 |
| dtbNa | $H_2O$ | | | | | | | | 20.8 (2.12) | | 28.2 (3.70) | 34.1 (3.63) |
| dtbH | $(C_2H_5)_2O$ | | | | | [g] | | | 19.0 (1.83) | | 30.0 (3.65) | 33.7 (3.98) |
| V(dtb)$_4$ | $CH_2Cl_2$ | 11.9 sh (2.40) | | 15.6 (3.08) | | 16.8 (3.09) | | 19.7 sh (>3.2) | | 23.5 sh (4.04) | | 32.8 (4.72) |
| | $C_6H_6$ | 11.8 sh (2.08) | | 15.7 sh (2.60) | | | | 19.6 sh (>3.2) | | 23.7 sh (4.78) | 26.0 sh (3.86) | 32.0 (4.92) |
| | Nujol[c] | 11.8 sh | | 15.2 sh | | 16.5 sh | | 19.0 sh ? | | 22.5 sh | 25.6 sh | 30.0 |
| | Nujol (77°K) | 11.8 sh | | 15.2 | | 16.2 sh | | 18.8 sh | | 22.2 sh | 25.9 sh | f |
| | e | f | | 15.1 | | 16.0 | | 19.7 | | 22.5 sh | f | f |
| dttNa | $H_2O$ | | | | | | | | 21.7 (2.22) | | 28.7 (3.77) | 32.1 (2.85) |
| dttH | $(C_2H_5)_2O$ | | | | | | | | 19.0 (1.72) | | | 32.4 (3.90) |
| V(dtt)$_4$ | $CH_2Cl_2$ | 12.5 sh (2.48) | | 15.6 (3.11) | | | | 19.2 sh (>3.0) | | 23.2 sh (4.08) | 28.4 sh | 31.2 (4.94) |
| | Nujol[c] | 12.5 | | 15.1 | | | | 19.6 sh | | 23.2 sh | 28.2 sh | 30.3 |
| | Nujol (77°K) | 12.8 | | 15.1 | | | | 19.3 sh | | 23.2 | f | f |

[a] Absorption maxima in kK. [b] sh = shoulder; log ε in parentheses. [c] Room temperature. [d] Very broad band; maximum frequency uncertain. [e] Single crystal. [f] Not measured beyond this frequency. [g] Transitions involving mixed metal and ligand orbitals (see text).

utable to these vibrations found in the spectra of the vanadium complexes.[28] Instead new bands appear at markedly lower and higher frequencies, respectively. This is consistent with



Thus we tentatively assign these new bands to the antisymmetric $\bar{\nu}_{as}$(CSS) and symmetric $\bar{\nu}_s$(CSS) stretching modes of the chelated ligands. Moreover, these frequencies are found in the same regions and often at the same energies as those assigned as $\bar{\nu}_{as}$ and $\bar{\nu}_s$ for the corresponding $NiL_2$ complexes, the residual features of the $VL_4$ and $NiL_2$ spectra being completely similar. This can be seen in Figure 1 for L = dtb$^-$.

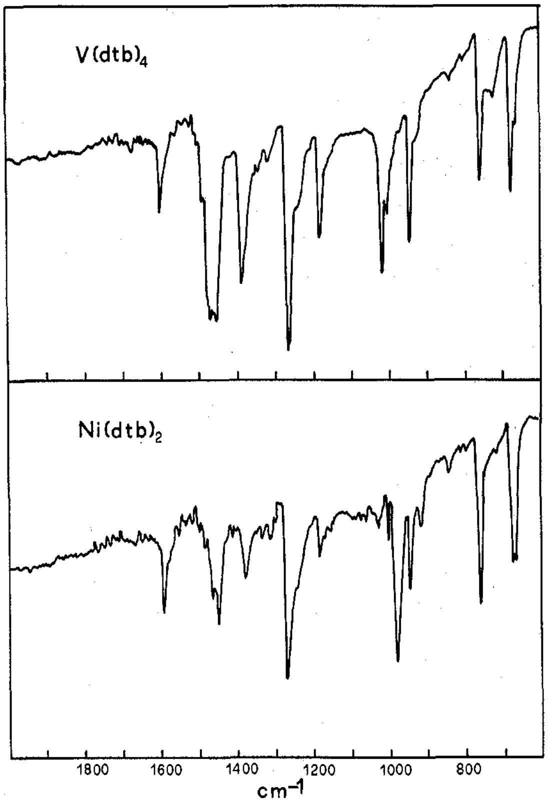


Figure 1.—Infrared spectra (Nujol mulls) of $V(dtb)_4$ and $Ni(dtb)_2$ in the region 2000–600 cm$^{-1}$.

Thus although there might be some doubt as to the exact assignment of the CSS modes,[20,22] mainly because of the complexity of ligand vibrations, the above arguments strongly suggest a chelated bidentate structure for each ligand in the vanadium dithiocarboxylato complexes.

This does not prove the existence of eight-coordination. In fact, a different coordination number could be achieved *via* a bridging as well as chelating character of some of the four dithiocarboxylato groups (see $U(CH_3COO)_4$[29]). The existence of the vanadium atom in monomeric units has been verified by molecular weight measurements in freshly prepared solutions in $C_2H_4Cl_2$ or $C_6H_6$. The close similarity of the electronic spectra of these solutions with those of either Nujol mulls or single crystals implies the presence of substantially the same species in the two media.

The molecular weights never indicated polymeric units. Indeed, except for $V(dtb)_4$, measured values were rather lower than the theoretical ones, suggesting that decomposition of the solutions, which is not completely avoidable, is connected with some dissociation reactions.

**Epr Spectra.**—Table IV and Figure 2 report epr results on the four vanadium dithiocarboxylates. These data indirectly confirm a +4 oxidation state for the central metal ion since V(V) has no unpaired electrons and V(III) usually does not give epr spectra, due to the high zero-field splitting.

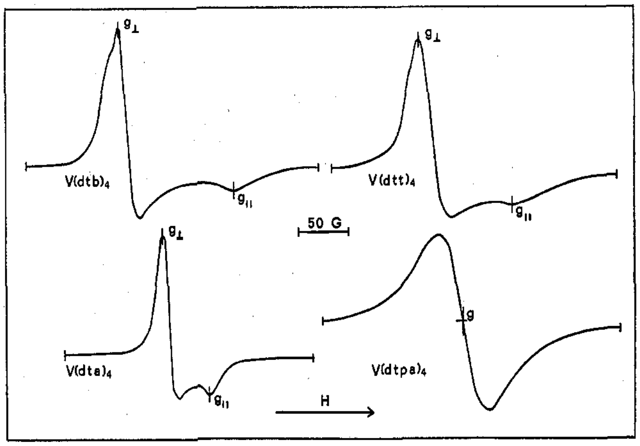


Figure 2.—Epr room-temperature powder spectra of the four $VL_4$ complexes.

Furthermore, the generally anisotropic signals rule out a regular octahedral or tetrahedral configuration and this confirms the suggestions of the infrared spectra. Magnetic measurements show, most clearly in $V(dtpa)_4$ and $V(dta)_4$, that there are no orbital angular momentum contributions (usually present for a $T_{2g}$ ground state). The epr spectra confirm this. Clearly the V(IV) atom is in a field of noncubic symmetry and this supports the view that it is eight-coordinated.

The factors determining the stereochemical configuration of an eight-coordinate compound have been variously stressed by different authors and no detailed prediction is possible to date.[30]

Valence-bond theory can be used qualitatively, in the present case, to restrict the choice of stereochemistry to two idealized structures, on the basis of the type of orbitals required to construct the proper set of hybridized orbitals directed from the vanadium atom to eight ligand atoms located at the corners of various ideal polyhedra.

Apart from the hendecahedron ($C_{2v}$ symmetry), which never has been observed for a "d$^n$" metal ion, only the dodecahedron ($D_{2d}$ symmetry) and the square antiprism ($D_{4d}$ symmetry) do not require the use of "f"-type orbitals.[30] Orbitals of this type are too high in energy to be involved in bonding in the case of vanadium.

Room-temperature powder spectra are interpreted

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[28] Previous assignment (O. Piovesana and C. Furlani, *Chem. Commun.*, 256 (1971)) of $\bar{\nu}_{as}$(CSS) at 1264 cm$^{-1}$ should be changed following ref 20.

[29] I. Jelenic, D. Grdenic, and A. Bezjak, *Acta Crystallogr.*, **17**, 758 (1964).

[30] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967), and references therein.

by the method of Kneubühl.[31] As can be seen from Figure 2, the spectrum of V(dtpa)$_4$ shows a broad, alalmost isotropic signal, while those of V(dta)$_4$, V(dtb)$_4$, and V(dtt)$_4$ clearly show axial symmetry with $g_\perp > g_\parallel$. $D_{4d}$ geometry requires that the V$^{4+}$ electron be in a d$_{z^2}$ orbital (A$_1$ symmetry), directed along the $\bar{8}$ axis. $D_{2d}$ geometry requires that the electron be in a d$_{x^2-y^2}$ orbital (B$_1$ symmetry), perpendicular to the $\bar{4}$ axis. Taking the magnetic field to be parallel to the $z$ axis, then for the antiprism $g_\parallel > g_\perp$ and for the dodecahedron $g_\parallel < g_\perp$.

The data for V(dta)$_4$, V(dtb)$_4$, and V(dtt)$_4$ clearly indicate that a $D_{2d}$ symmetry is present. For V(dtpa)$_4$ magnetic exchange phenomena are probably important and asymmetry is evident from the broadness of the band; lower temperatures are probably needed to observe splitting of the $g$ parameter. In fact, a preliminary X-ray investigation by Bonamico, *et al.* (*vide infra*), shows an approximately dodecahedral structure for this molecule. A more detailed epr investigation is in progress and will be discussed in a subsequent paper.

**X-Ray Analyses.**—The evidence so far accumulated for the existence of VS$_8$ chromophores and their geometry in the four V(IV) dithiocarboxylato complexes, at least in two cases, is unambiguously verified by the preliminary results of two X-ray analyses, carried out on V(dtpa)$_4$[32] and V(dta)$_4$.[33] The vanadium atom was found to be coordinated to eight sulfur atoms in these complexes, as shown in Figure 3 and ref 32.

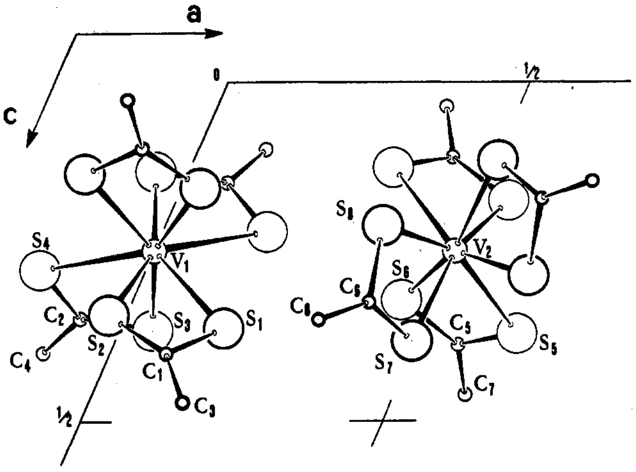

Figure 3.—The V(dta)$_4$ structure projected along the $b$ axis. V$_1$ and V$_2$ are the two independently coordinated vanadium atoms in the unit cell.[34]

In a dodecahedral coordination, the metal atom position, at the center of the polyhedron, has $D_{2d}$-$\bar{4}2m$ site symmetry. The eight donor atom sites are equally divided into symmetry-equivalent sets of four, A and B, respectively, comprising two interpenetrating bisphenoids. In order to specify the shape of the dodecahedron three parameters are required: the angles $\theta_A$ and $\theta_B$, which the bonds M–A and M–B make with the unique axis, and the ratio of the bond lengths $R_A/R_B$. According to Hoard and Silverton,[34] the "most favorable parameters" should be $\theta_A = 35.2°$, $\theta_B = 73.5°$, and $R_A/R_B = 1.03$.

In V(dtpa)$_4$ the experimental shape parameters are found to be $\theta_A = 37.6°$, $\theta_B = 76.0$, and $R_A/R_B = 1.02$, the $D_{2d}$-$\bar{4}2m$ symmetry being nearly achieved in the VS$_8$ chromophore (belonging to *Id* subclass).[32]

In V(dta)$_4$ two independently coordinated vanadium atoms V(1) and V(2) comprise the asymmetric unit in the elementary cell. The arrangement of the eight sulfur atoms around V(1) is specified by $\theta_A = 35.1°$, $\theta_B = 77.0°$, and $R_A/R_B = 1.02$, and that around V(2) is specified by $\theta_A = 38.0°$, $\theta_B = 70.0°$, $R_A/R_B = 1.02$. The V(1) complex belongs to *Id* subclass, while the V(2) stereoisomer belongs to *Vd* subclass.[33]

The two $\bar{4}$ axes lie in a plane parallel to the *ac* plane and make an angle of about 70°.[33]

(B) **Electronic Spectra.**—Details of the electronic spectra of the four vanadium dithiocarboxylato complexes are in Table V. The absorption maxima of the free ligands are also shown for comparison.

The general shape of the spectra of the complexes is dominated by a very high-intensity, broad absorption in the near-uv region. This masks the bands in the lower energy regions, which are observable only as shoulders in many cases. There is no resolution at low temperature and the molar extinction coefficients are inaccurate.

Spectra measured both on single crystals (for which better resolution is achieved) and on Nujol mulls resemble those of freshly prepared solutions in nonpolar solvents. (See Figures 4 and 5 for pertinent spectra.)

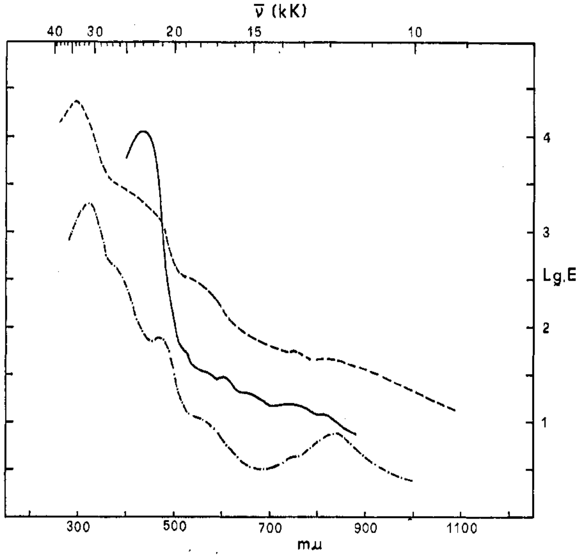

Figure 4.—Absorption spectra: —, V(dta)$_4$, single crystal; — — —, V(dtpa)$_4$ in CH$_2$Cl$_2$; —·—·—, V(dtpa)$_4$ in Nujol mull at 77°K.

The nature of the solvent appears to influence the intensity of the bands. The present experimental information is not sufficient for determining whether these changes are simply connected with a different resolution of the bands or to some slight stereochemical modification. Spectra of aged solutions show marked deviations from solid-state spectra.

Despite uncertainty as to the exact location of the absorption maxima and their intensity, the general

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[31] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[32] M. Bonamico, G. Dessy, V. Fares, P. Porta, and L. Scaramuzza, *Chem. Commun.*, 365 (1971).

[33] L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, submitted for publication in *Acta Crystallogr.*

[34] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

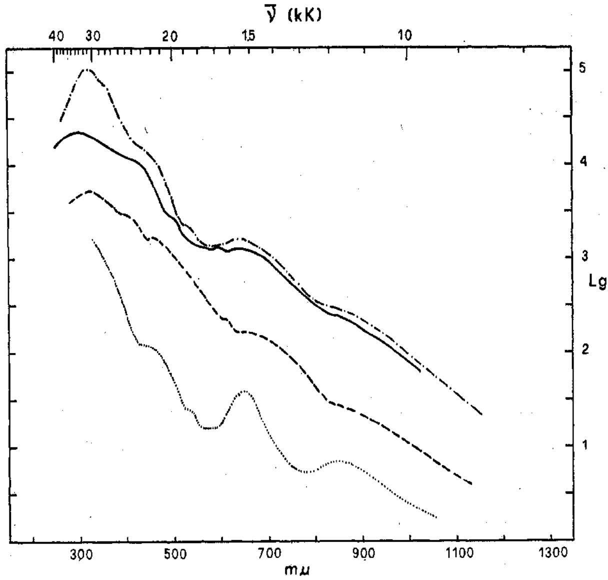

Figure 5.—Absorption spectra: —, V(dtb)$_4$ in $CH_2Cl_2$; — — — —, V(dtb)$_4$ in Nujol mull; —·—·, V(dtt)$_4$ in $CH_2Cl_2$; ··········, V(dtt)$_4$ in Nujol mull at 77°K.

patterns of the spectra lead to a relatively simple classification.

(1) Bands between $\sim$30 and $\sim$34 kK are due to intraligand transitions. Similar bands are found in dithiocarboxylato complexes of other metals and have already been assigned to $\pi \rightarrow \pi^*$ transitions.[21,24,35–37]

(2) One or two very intense bands (shoulders) are present for each complex at about 22 and 27 kK, respectively, and are most probably charge transfer in origin, in view of their intensity. A much less intense band is present in the free ligands at about the same frequency as the lower frequency band in the complexes, but its assignment could be hardly the same since in the free ligands it corresponds to an $n \rightarrow \pi^*$ transition localized on the C=S group,[21,24,36] which should be found at sensibly different energy when the sulfur atoms are coordinated. For the bands at $\sim$27 kK, a CT state could possibly be mixed with a $\pi \rightarrow \pi^*$ state.

(3) For each complex, several bands are observed between $\sim$12 and $\sim$20 kK, *i.e.*, the region in which d–d transitions are expected. $VCl_4 \cdot 2diars$[38] and $V(S_2CNEt_2)_4$,[3] the only previously known eight-coordinate V(IV) complexes, exhibit d–d bands at 13.2 and 15.6 kK, respectively. The intensity of these bands is strongly dependent on the nature of the ligand substituents; *i.e.*, it is strongly increased on going from aliphatic- or aryl–aliphatic- to aryl-substituted dithiocarboxylato complexes.

While the bands between $\sim$12 and $\sim$20 kK in V(dta)$_4$ and V(dtpa)$_4$ can reasonably be assigned as mainly d–d bands, the higher intensity of the corresponding bands in V(dtb)$_4$ and V(dtt)$_4$, except possibly that at $\sim$13 kK, points to strong mixing of the metal and ligand valence orbitals. A ligand field description is inadequate in such cases and assignment of the bands may be made only by complete MO calculations. A similar situation is found in Ni(dtb)$_2$ and Ni(dtt)$_2$[21,24] and has tentatively been related to the extension of $\pi$ conjugation over both the CSS group and the phenyl ring.[24]

TABLE VI

ENERGIES OF THE VANADIUM d ORBITALS AS FUNCTIONS OF *Dq* AND *Cp*

| | V(dtpa)$_4$ | V(1)(dta)$_4$ | V(2)(dta)$_4$ |
|---|---|---|---|
| $d_{x^2-y^2}$ | $-5.3342Dq - 0.2364Cp$ | $-5.1011Dq - 0.4442Cp$ | $-5.0339Dq - 0.5260Cp$ |
| $d_{z^2}$ | $-0.7815Dq + 0.2364Cp$ | $+0.0387Dq + 0.4442Cp$ | $-2.0366Dq + 0.5260Cp$ |
| $d_{xz,yz}$ | $+0.5210Dq + 0.0979Cp$ | $-0.0258Dq + 0.2019Cp$ | $+1.3577Dq + 0.2458Cp$ |
| $d_{xy}$ | $+5.0732Dq - 0.2364Cp$ | $+5.1139Dq - 0.4442Cp$ | $+4.3551Dq - 0.5260Cp$ |

The relative d-orbital energies of transition metal ions in eight-coordinate complexes with $D_{2d}$ symmetry have recently been calculated using a point-charge model.[39] These energies were shown to be sensitive to the detailed geometry assumed (values of $R_A/R_B$, $\theta_A$, $\theta_B$) and also to the crystal-field parameters *Dq* and *Cp*. A point-charge model is of limited validity in cases such as the present one. However, because of its simplicity, it is of interest to attempt a qualitative fit of the spectra of V(dtpa)$_4$ and V(dta)$_4$, for which d–d bands can be identified with greater confidence and the $R_A/R_B$, $\theta_A$, and $\theta_B$ parameters are known from X-ray work. The energies of the vanadium d orbitals in V(dtpa)$_4$ and in the two independently coordinated vanadium atoms (V(1) and V(2)) in V(dta)$_4$, calculated using the algebraic expressions given by Garner and Mabbs,[39] are reported in Table VI, as functions of *Dq* and *Cp*. In all three cases, $d_{x^2-y^2}$ is the lowest lying d orbital, in agreement with the epr spectra. In V(dtpa)$_4$ the relative ordering of the d-orbital energies, for any *Cp*/*Dq* ratio between 2 and 8 (which are the approximate limits for a wide range of first-row transition metal ions and metal–ligand distances),[40] is $d_{x^2-y^2} < d_{z^2} < d_{xz,yz} < d_{xy}$. According to this scheme, the spectrum of V(dtpa)$_4$ should show three d–d bands, that at highest frequency being attributable to the $d_{x^2-y^2} \rightarrow d_{xy}$ transition, the energy of which is a function only of *Dq*.

From Table VI it can be seen that if an energy of 19 kK is assigned to $d_{x^2-y^2} \rightarrow d_{xy}$, a *Dq* value of 1826 cm$^{-1}$ is obtained, which gives a *Cp* value of 9897 cm$^{-1}$ if an energy of 14 kK is assigned to $d_{x^2-y^2} \rightarrow d_{xz,yz}$. Using the experimental ratio $Cp/Dq = 5.4$, a frequency of 12.99 kK is calculated for the third transition $d_{x^2-y^2} \rightarrow d_{z^2}$. This result is matched by the presence of the band at $\sim$12.5 kK.

A more complicated d–d spectrum is predicted for solid V(dta)$_4$, due to the presence of two independent vanadium atoms in the unit cell. Assuming the same

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

(36) M. Bossa, *J. Chem. Soc. B*, 1182 (1969).

(37) A. Flamini, C. Furlani, and O. Piovesana, *J. Inorg. Nucl. Chem.*, **33**, 1841 (1971).

(38) P. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2460 (1962).

(39) C. D. Garner and F. E. Mabbs, *J. Chem. Soc. A*, 1711 (1970).

(40) C. Ballhausen and E. M. Ancon, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **31**, 3 (1958).

ratio, $Cp/Dq = 5.4$, as found for V(dtpa)$_4$ the sequences obtained are as follows: V(1), $d_{x^2-y^2} < d_{xz,yz} < d_{z^2} < d_{xy}$; V(2), $d_{x^2-y^2} < d_{z^2} < d_{xy} < d_{xz,yz}$.

Room-temperature Nujol mull spectra of V(dta)$_4$ show only two very broad shoulders at ~12 and ~19 kK. Better resolved single-crystal spectra show numerous shoulders in the region in which d–d transitions are expected, giving an at least qualitative agreement with the above scheme. Single-crystal polarized spectra and epr spectra are planned in order to give a more detailed description of the electronic structure of the complexes described.

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# Transition Metal Eight-Coordination. IV. Tetrakis(5,7-disubstituted-8-quinolinolato)tungsten(V) Salts[1]

BY RONALD D. ARCHER,* WESLEY D. BONDS, JR., AND ROBERT A. PRIBUSH

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Violet, paramagnetic $[WQ_4]^+$ ions have been synthesized by a variety of methods and appear to be the first complexes of tungsten(V) possessing four chelate ligands. The 5,7-dichloro-8-quinolinol derivative has been synthesized by the reaction of either $K_3W_2Cl_9$ or $W(CO)_6$ with excess ligand at elevated temperatures for extended time periods or by treating the corresponding tungsten(IV) inner complex with $Cl_2$, $Br_2$, or $HClO_4$ at room temperature or with additional ligand at elevated temperatures. The 7-bromo-5-methyl-8-quinolinol–tungsten(V) species is rapidly produced in the melt reaction of the ligand with $W(CO)_6$. The $[WQ_4]X$ salts, where $X^- = Cl^-$, $Br^-$, $ClO_4^-$, or $Q^-$, disproportionate in alcoholic or aqueous KOH to $WQ_4$ and tungsten(VI). Electronic transitions of the $[WQ_4]$ species consist of several bands in the near-infrared and visible region in addition to the normal ligand spectral transitions. A magnetic moment of 1.7 BM, a $\langle g \rangle$ value of 1.872, and a $^{183}W$ hyperfine splitting of 85 G were observed for the dichloro derivative at room temperature. Low-temperature electron spin resonance spectra exhibit three anisotropic $g$ values indicative of isomerization from the *D*$_{2d}$-*mmmm* isomer found for a related 5-bromo-8-quinolinol–tungsten(IV) chelate.[1a]

## Introduction

Well-defined, eight-coordinate complexes of the transition elements in which the same element occurs in two oxidation states are indeed rare.[2] Eight-coordinate cations are also relatively scarce.[2,3] We have previously isolated $WQ_4$-type species, where $Q^-$ is the anion of an 8-quinolinol derivative.[4] We wish to report the isolation of $[WQ_4]X$ salts, where $X^-$ is $Cl^-$, $Br^-$, or $ClO_4^-$. The molybdenum(V) and -(IV) and tungsten(V) and -(IV) octacyano series are the only other eight-coordinate d$^1$ and d$^2$ pairs known.[5] Whereas the octacyanomolybdenum(IV) complex appears more stable than the molybdenum(V) species, the octacyanotungsten(V) complex is of comparable stability with the tungsten(IV) complex.[6] Furthermore, recent X-ray results[7] with the octacyano complexes show that dodecahedral and antiprismatic configurations are both accessible for identical $ML_8^{n-}$ species. Whether this is true of complexes with different ligands or chelates with unequal donors, such as the $WQ_4$ and $[WQ_4]^+$ complexes, is unknown. The dodecahedral configuration has been found for tetrakis(5-bromo-8-quinolinolato)tungsten(IV)–benzene,[1a] the only chelate of these series for which suitable, untwinned crystals have been obtained to date.

## Results

**Synthesis.**—Reactions which lead to the tetrakis(5,7-dichloro-8-quinolinolato)tungsten(V) ion include (where $QCl_2^-$ = the anion of 5,7-dichloro-8-quinolinol)

$$W_2Cl_9{}^{3-} \xrightarrow[\text{melt}]{HQCl_2} W(QCl_2)_4 \longrightarrow [W(QCl_2)_4](QCl_2) \quad (1)$$

$$W(CO)_6 \xrightarrow[\text{melt}]{HQCl_2} W(QCl_2)_4 \longrightarrow [W(QCl_2)_4](QCl_2) \quad (2)$$

$$W(QCl_2)_4 \xrightarrow[CCl_4]{Cl_2} [W(QCl_2)_4]Cl \quad (3)$$

$$W(QCl_2)_4 \xrightarrow[CCl_4]{Br_2} [W(QCl_2)_4]Br \quad (4)$$

$$W(QCl_2)_4 \xrightarrow[CH_2Cl_2\text{–}C_2H_5OH]{72\%\ HClO_4} [W(QCl_2)_4](ClO_4) \quad (5)$$

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[1] (a) Part III: W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, **10**, 1764 (1971). (b) Abbreviations: $HQCl_2$ = 5,7-dichloro-8-quinolinol; HQBrMe = 7-bromo-5-methyl-8-quinolinol; HQAc = 5-acetyl-8-quinolinol; HQBr = 5-bromo-8-quinolinol; $HQClNO_2$ = 7-chloro-5-nitro-8-quinolinol, etc.; HQ = 8-quinolinol and its derivatives in general. (c) Abstracted in part from the Ph.D. dissertation of W. D. B., University of Massachussetts, 1970.

[2] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

[3] (a) D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Lett.*, **6**, 187 (1970), and (b) R. L. Bodner and D. G. Hendricker, *ibid.*, **6**, 421 (1970), have recently synthesized an extensive series of labile complexes with 1,8-naphthyridine which are eight-coordinate: (c) A. Clearfield, P. Singh, and I. Bernal, *J. Chem. Soc. D*, 389 (1970).

[4] (a) R. D. Archer and W. D. Bonds, Jr., *J. Amer. Chem. Soc.*, **89**, 2236 (1967); (b) W. D. Bonds, Jr., and R. D. Archer, *Inorg. Chem.*, **10**, 2057 (1971).

[5] In addition to ref 2, reviews considering eight-coordinate complexes include (a) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963); (b) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967); (c) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966); (d) J. S. Wood, *ibid.*, **2**, 403 (1967); and earlier references such as (e) L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Amer. Chem. Soc.*, **65**, 329 (1943).

[6] (a) A. Samotus and B. Kosowicz, *Proc. Int. Conf. Coord. Chem., 12th*, 211 (1969); (b) A. Samotus, *Proc. Int. Conf. Coord. Chem., 13th*, **2**, 287 (1970).

[7] (a) B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970). (b) L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Acta Crystallogr., Sect. B*, **26**, 684 (1970), present distorted dodecahedral and antiprismatic structures for the $[W(CN_8)]^{3-}$ ion. Antiprismatic coordination for the corresponding d$^2$ ions has also been observed [(c) J. Chojnacki, J. Grochowski, L. Lebioda, B. Oleksyn, and K. Stadnicka, *Rocz. Chem.*, **43**, 273 (1969); (d) S. S. Basson, L. D. C. Bok, and J. G. Leipoldt, *Acta Crystallogr. Sect. B*, **26**, 1209 (1970)] even though the classical structure is known to be dodecahedral: (e) J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, **61**, 2853 (1939); *cf.* (f) J. L. Hoard, T. A. Hamor, and M. D. Glick, *ibid.*, **90**, 3177 (1968).