k_2/k_1 limits $k_{-\mathrm{CH_3OH}}/k_{-\mathrm{H_2O}}$ to a maximum value of 1.5 from eq 7. This in turn limits the second term to a value less than 0.1. The data for the chloride system for k_2/k_1 with the value of 1.5 equal to $k_{-\mathrm{CH_3OH}}/k_{-\mathrm{H_2O}}$ limit the second term to a value of 2.0. The value of $k'_{+\mathrm{X}^-}/k_{+\mathrm{X}^-}$ is the only variable at constant solvent composition in the second term of eq 7 when $k_{+\mathrm{H_2O}}\cdot a_{\mathrm{H_2O}} + k_{+\mathrm{CH_3OH}}a_{\mathrm{CH_3OH}} > k_{+\mathrm{X}^-}/\mathrm{X}^-]$ and $k'_{+\mathrm{H_2O}}\cdot a_{\mathrm{H2O}} > k'_{+\mathrm{X}^-}[\mathrm{X}^-]$. The implication is that the rate coefficients $k'_{+\mathrm{X}^-}$ and $k_{+\mathrm{X}^-}$ show considerable dependence upon the entering group. Differences between $k'_{+\mathrm{Cl}^-}$ and $k'_{+\mathrm{SCN}^-}$ are expected in limiting SN1 mechanisms. Halpern[10] and Haim and Wilmarth[11] found evidence of a limiting SN1 mechanism in some cobalt(III) complexes where the reactivity of the intermediate followed the order $\mathrm{OH}^- > \mathrm{CN}^- > \mathrm{SCN}^- > \mathrm{Br}^-$. However, the dependence of the ratio $k'_{+\mathrm{X}^-}/k_{+\mathrm{X}^-}$ upon entering group is not expected. The thermodynamic stabilities of chloromethanoltetraaquochromium(III) and chloropentaaquochromium(III) ions relative to hexaaquochromium(III) and methanolpentaaquochromium(III) are identical.[3] If the rate coefficients follow the thermal stability, then the ratio $k'_{+\mathrm{X}^-}/k_{+\mathrm{X}^-}$ should be near unity. The evidence indicates that all of the reactions do not proceed through a five-coordinated intermediate. If medium effects are unimportant, then argument can be made that all values of k_2/k_1 must be greater than 3.3 to be consistent with a limiting SN1 mechanism. If medium effects are important, the dependence of $k'_{+\mathrm{X}^-}/k_{+\mathrm{X}^-}$ on the entering group is not consistent with a limiting SN1 mechanism.

The kinetic data are consistent with the interchange mechanism described in eq 8 and 9, but there is an obvious dependence of the rate coefficients upon the entering group. The ligand dependence of the ratio k_2/k_1 is very interesting and it appears to be very worthwhile to perform additional experiments particularly on the acid dependence of the rates and ratio of the various products in the reactions. Several authors have discussed the dependence of rate upon the entering group.[12] The reactions can be associative in nature[13] or the proton transfer to the anion in an ion interchange transition state could make the entering group become HX in place of X^-.[12,14]

The study has shown that the methanol catalysis of the substitution reaction of chromium(III) with thiocyanate is not as great as in the chloride case, but still an important factor in measuring rate coefficients in mixed solvents. The value of k_1 measured in water agrees with a previous study of Postmus and King in which a value of k_f $(=k_1 + k_2[\mathrm{H}^+]^{-1} + k_3[\mathrm{H}^+]^{-2})$ is $2 \times 10^{-6}\ M^{-1}\ \mathrm{sec}^{-1}$ in 0.1 M hydrogen ion concentration and in ionic strength of 0.600 M at 25°. In 0.1 M hydrogen ion 96% of the reaction goes by the acid-independent step.[13]

(10) J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

(11) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

(12) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(13) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

(14) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KENTUCKY, LEXINGTON, KENTUCKY 40506

Complexes with Sulfur and Selenium Donors. I. Tris(O,O′-dialkyldithiophosphato)-chromium(III) Compounds

BY JOHN R. WASSON,[1a] SHIRLEY J. WASSON,[1b]
AND GERALD M. WOLTERMANN

Received December 8, 1969

A wide variety of complexes with sulfur and selenium donor atoms has been described[2] and such compounds continue to be of considerable interest.[3] O,O′-Dialkyldithiophosphoric acids have long been known to form highly colored complexes with transition metal ions. Of these, complexes of O,O′-diethyldithiophosphoric acid (Et-dtp) have undoubtedly been the most extensively investigated.[4-8] The electronic spectrum of $\mathrm{Cr(Et\text{-}dtp)_3}$ has shown that Et-dtp should be placed below water in the spectrochemical series.[7] However, the very low value for the nephelauxetic parameter,[9] β, and the appreciable intensities[7,9] of the electronic absorption bands of $\mathrm{Cr(Et\text{-}dtp)_3}$ are indicative of considerable metal–ligand covalency. The high degree of covalency of metal ion–O,O′-dialkyldithiophosphate bonds is also demonstrated by the observation of the $^{31}\mathrm{P}$ superhyperfine splitting in the electron spin resonance (esr) spectra of oxovanadium(IV) and copper(II) chelates.[10] As there are slight, albeit not dramatic, changes in the pK_a's of O,O′-dialkyldithiophosphoric acids with substituent variations,[11] the spectral and magnetic properties of a series of tris(O,O′-dialkyldithiophosphato)chromium(III) compounds were prepared and characterized in order to determine the effects of substituent variation and to document further the properties of complexes with dithiophosphate ligands.

Experimental Section

Phosphorus(V) sulfide was obtained from Matheson Coleman and Bell, Norwood, Ohio. All other chemicals were of the best available reagent or spectroscopic grade. Carbon and hydrogen

---

(1) (a) Author to whom correspondence should be addressed. (b) National Science Foundation college teacher summer research participant, Illinois Institute of Technology, Chicago, Ill., 1969.

(2) S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

(3) (a) V. Krishnan and R. A. Zingaro, *Inorg. Chem.*, **8**, 2337 (1969); (b) S. L. Lawton and G. T. Kokotailo, *ibid.*, **8**, 2410 (1969).

(4) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 131.

(5) A. Sgamellotti, C. Furlani, and A. Magrini, *J. Inorg. Nucl. Chem.*, **30**, 2655 (1968).

(6) P. S. Shetty and Q. Fernando, *ibid.*, **28**, 2873 (1966); Q. Fernando and C. D. Green, *ibid.*, **29**, 647 (1967); S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967); J. F. McConnell and V. Kastalsky, *Acta Cryst.*, **22**, 853 (1967).

(7) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(8) S. Gregorio, J. Weber, and R. Lacroix, *Helv. Phys. Acta*, **38**, 172 (1965); N. S. Garif'yanov, B. M. Kozyrev, and S. Z. Luchkina, *Zh. Strukt. Khim.*, **9**, 901 (1968).

(9) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962); *Advan. Chem. Phys.*, **5**, 33 (1963).

(10) J. R. Wasson, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

(11) T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Am. Chem. Soc.*, **67**, 1662 (1945); M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, **9**, 10 (1960).

analyses were obtained by Mr. Daryl G. Sharp of the department analytical services. See Table I for analytical data.

TABLE I

ANALYTICAL DATA FOR $Cr(S_2P(OR)_2)_3$ COMPLEXES

R	% calcd C	% calcd H	% found C	% found H
Methyl	13.77	3.47	13.21	3.54
Ethyl	23.72	4.98	24.01	5.10
n-Propyl	31.25	6.12	30.36	6.12
Isopropyl	31.25	6.12	30.52	6.09
sec-Butyl	37.15	7.01	37.20	6.94
Isobutyl	37.15	7.01	36.91	7.08

The O,O′-dialkyldithiophosphate complexes were prepared by adding finely ground chromium(III) chloride hexahydrate to the acid obtained from the alcoholysis of phosphorus(V) sulfide.[11] The preparations were carried out in essentially the same manner as that described for the diethyl complex.[12] The dark purple methyl, ethyl, *n*-propyl, isopropyl, *sec*-butyl, and isobutyl complexes were recrystallized several times from chloroform.

Electronic absorption spectra were obtained with a Cary Model 15 recording spectrophotometer using matched 1.0-cm quartz cells. Infrared spectra (4000–200 cm^{-1}) were measured with a Perkin-Elmer 621 instrument using Nujol and Fluorolube (Hooker Chemical Co.) mulls in sodium chloride and cesium iodide cells. Electron spin resonance spectra of finely ground compounds were obtained using the X-band instrument and techniques previously described.[13] Magnetic susceptibilities at ambient room temperature were determined by both the Gouy and Evans[14] methods. Mass spectra were obtained using a double-focusing Hitachi Perkin-Elmer RMU-7 spectrometer. Routine spectra were run with a resolution of about 2000 with the ionization energy maintained at approximately 70 eV.

Results and Discussion

The ready solubility and similar spectra of the O,O′-dialkyldithiophosphate complexes in a wide variety of organic solvents is indicative of the monomeric nature of the complexes. The mass spectra of the complexes revealed no ions with masses greater than the molecular weights of monomers. The molecular ion was observed for all of the compounds. The fragmentation patterns show that the chelate rings are not broken up until most of the alkyl groups are lost. Apparently, the chromium–sulfur bonds are stronger than the oxygen–alkyl linkages. These results are consistent with more detailed mass spectral studies of O,O′-dialkyldithiophosphate complexes now in progress.[15]

The magnetic moments of the chromium(III) dithiophosphate complexes, $Cr(R\text{-}dtp)_3$, were close (±0.07 BM) to the value (μ(spin only) = 3.87 BM) expected for systems containing three unpaired electrons. The esr spectra of powdered samples of the methyl, ethyl, and *n*-propyl derivatives consisted of a single broad line with a peak to peak separation on the order of 300 G and a g value of 1.980 ± 0.010. Assuming effective octahedral geometry the average g values for chromium(III) complexes are given by[16]

$$\langle g \rangle = 2.0023(1 - 4\lambda'/\Delta) \qquad (1)$$

where Δ $(= 10Dq)$ is the ligand field splitting parameter and λ' is the effective spin–orbit coupling constant for the metal ion in the complex. Owen[17] noted previously that the reduction of the spin–orbit coupling constant from the free-ion value can be employed as a measure of metal–ligand covalency. Taking Δ = 14,500 cm^{-1} (see following discussion of electronic spectra), λ' = 40 cm^{-1} for $Cr(R\text{-}dtp)_3$ complexes, a value some 56% below the free-ion value of 90 cm^{-1}. This measure of covalency is in accord with the electronic transition strengths and nephelauxetic parameters discussed below.

The electronic spectra of $Cr(R\text{-}dtp)_3$ complexes (Figure 1) have two strong absorption bands in the visible region. The ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$ transition, expected to appear at about 30,870 cm^{-1}, is not observed due to intense charge-transfer bands in the ultraviolet region. The electronic absorption spectra of $Cr(R\text{-}dtp)_3$ complexes along with band assignments and B values are listed in Table II. The oscillator strengths, f, an additional measure of covalency, are also tab-

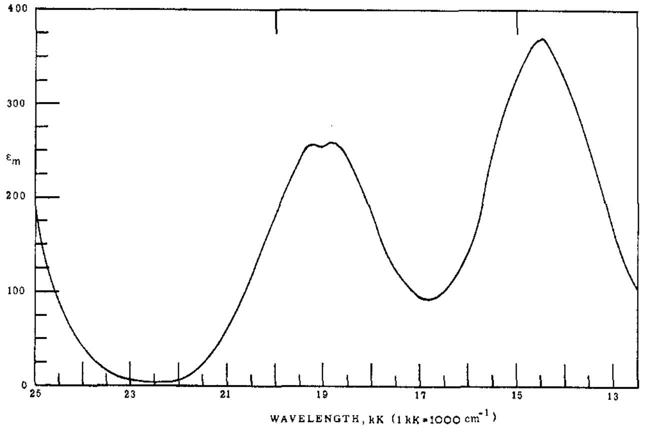

Figure 1.—Electronic absorption spectrum of tris(O,O′-dimethyldithiophosphato)chromium(III) in chloroform. The 0.4-kK splitting of the 19-kK band is due to the trigonal component of the ligand field.

TABLE II

VISIBLE SPECTRA OF $Cr(S_2P(OR)_2)_3$ COMPLEXES IN CHLOROFORM

R	ν_1, cm^{-1}	ϵ_m [a]	$10^5 f_1$ [b]	ν_2, cm^{-1}	ϵ_m	$10^5 f_2$	B,[c] cm^{-1}
Methyl	14,450	372	474	19,050	255	360	434
Ethyl	14,470	353	452	19,100	247	354	427
n-Propyl	14,430	371	481	19,010	267	383	432
Isopropyl	14,470	348	454	19,050	250	353	432
sec-Butyl	14,490	336	429	19,050	251	350	418
Isobutyl	14,450	358	460	19,050	256	359	444
Methyl[d]	14,450	333	437	19,050	232	337	434
Methyl[e]	14,490	344	458	19,010	234	364	424

[a] Molar absorption coefficient. [b] Oscillator strengths, f, were calculated using the expression $f = 4.60 \times 10^{-9}\epsilon_{max}\nu_{1/2}$ where ϵ_{max} is the molar absorptivity of the band maximum and $\nu_{1/2}$ is the band width at half-height expressed in wave numbers: C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960). [c] The Racah interelectronic repulsion parameter, B, was calculated using the expression $B = (2\nu_1^2 - 3\nu_1\nu_2 + \nu_2^2)/(15\nu_2 - 27\nu_1)$. [d] N,N′-Dimethylformamide solution. [e] Acetone solution.

---

(12) D. E. Goldberg, W. C. Fernelius, and M. Shamma, *Inorg. Syn.*, **6**, 142 (1960).

(13) J. R. Wasson, C. I. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

(14) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); J. L. Deutsch and S. M. Poling, *J. Chem. Educ.*, **46**, 167 (1969).

(15) C. Reichert and R. W. Kiser, personal communication.

(16) J. W. Orton, "Electron Paramagnetic Resonance," Iliffe Books Ltd., London, 1968, pp 113 and 140.

(17) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

TABLE III

SPECTROSCOPIC PARAMETERS FOR COMPLEXES CONTAINING THE $Cr^{III}S_6$ CHROMOPHORE[a]

	Dq, cm^{-1}	B, cm^{-1}	β_{35}	$\epsilon_m(\nu_1)$	$\epsilon_m(\nu_2)$	$\nu_2 - \nu_1$, cm^{-1}
Cr(R-dtp)$_3$	1445	418–434	0.45–0.48	~350	~255	4540–4600
Cr(dtc)$_3$[b]	1550	457	0.50	380	360	4860
$Cr(S_2CNH_2)_3$[b]	1550	426	0.46	310	310	4500
Cr(xan)$_3$[b]	1612	403	0.44	...	...	4380
$KCa(Cr(S_2C_2O_2)_3)\cdot 6H_2O$[c]	1700	454	0.50	435	1028	4900
$((C_3H_7)_4N)_3$(Cr(*i*-mnt)$_3$)[d]	1515	487	0.53	360	500	5100
Cr(MTU)$_6$(ClO$_4$)$_3$[e]	1450	423	0.46	...	...	4500
Cr(DMTU)$_6$(ClO$_4$)$_3$[e]	1400	487	0.53	...	...	4200

[a] Dq and B for all compounds were calculated using strong octahedral field matrices: R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6,** 1338 (1967). [b] dtc = diethyldithiocarbamate, xan = ethylxanthate. Spectral data were taken from ref 7. [c] R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40,** 371 (1964). [d] *i*-mnt = $S_2C_2(CN)_2^{2-}$: J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88,** 3913 (1966); D. Coucouvanis, *Progr. Inorg. Chem.*, in press. [e] MTU = N-methylthiourea; DMTU = N,N′-dimethylthiourea: P. Askalani and R. A. Bailey, *Can. J. Chem.*, **47,** 2275 (1969).

ulated. Table III compares the spectroscopic properties of a number of compounds containing the $Cr^{III}S_6$ chromophore. It should be noted that the octahedral polymers Cr(SR)$_3$ (R = methyl, ethyl, phenyl, benzyl) reported by Brown and coworkers[18] are not included in Table III; reasonable values of B could not be calculated using the reported spectra.

Table II shows that there is essentially no substituent effect on the spectroscopic properties of the complexes. This demonstrates that the properties of the complexes are predominantly determined by the CrS_2P chelate rings. The Dq value for dithiophosphate ligands places them below water (Dq = 1740 cm^{-1}) in the spectrochemical series for chromium(III). This result is not in conflict with the inference of strong metal–ligand covalency from esr data if it is noted that the electronic spectra of complexes are a function of Dq *and* Racah interelectronic repulsion parameters and not just Dq alone. The large values of the oscillator strengths of the electronic transitions, indicative of extensive metal–ligand delocalization, must be interpreted with some caution. Although the transition energies can be treated reasonably well in terms of an O_h model, the band intensities of chromium(III) complexes are a rather sensitive function of molecular geometry. On going from complexes conforming fairly well to octahedral geometry to those with D_3 symmetry, which is expected for Cr(R-dtp)$_3$ complexes, the oscillator strengths increase two- to fivefold due to loss of the center of inversion. The oscillator strengths of Cr(R-dtp)$_3$ complexes attain their magnitudes through operation of both symmetry and covalency effects, the latter probably being the more significant as low nephelauxetic parameters and esr data would suggest.

Table III shows that there is a great similarity in the spectroscopic properties of complexes containing the $Cr^{III}S_6$ chromophore although the Dq values range from 1400 to 1700 cm^{-1}. The β_{35} values are indicative of strong covalency in the metal–ligand σ bonds.[8] The nephelauxetic parameters, β_{55}, obtained from a consideration of low-energy quartet–doublet transitions[8] are also consistent with appreciable Cr–S π bonding in complexes containing $Cr^{III}S_6$ chromophores.

In the 400–200-cm^{-1} region of the infrared spectra the Cr(R-dtp) complexes exhibit a strong band near 318 cm^{-1} and two bands of medium to weak intensity near 356 and 397 cm^{-1}. These bands are in the region 440–200 cm^{-1} assigned to predominantly metal–sulfur stretching frequencies of sulfur-donor chelates[19] and are independent of the alkyl substituents in the Cr(R-dtp)$_3$ compounds. The observed bands are tentatively identified with chromium(III)–sulfur stretching frequencies until more extensive studies of the infrared and Raman spectra of these and complexes with other metal ions are completed.

Acknowledgments.—Initial work was performed at Illinois Institute of Technology, Chicago, Ill. The authors are grateful to Dr. Charles Trapp for the use of the esr instrument, to Dr. Charles Reichert for discussions of the mass spectral data, and to Mr. Claude Dungan for obtaining the mass spectra. The Perkin-Elmer 621 instrument was purchased with funds made available by the University of Kentucky Major Research Equipment Fund.

(18) D. A. Brown, W. K. Glass, and B. Kumar, *J. Chem. Soc., A*, 1510 (1969).

(19) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold (Publishers) Ltd., London, 1967, p 319.

CONTRIBUTION NO. 1794 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

The Reaction of Silicon Tetrachloride and Silane with Small Carbon Molecules

BY JEHUDA BINENBOYM AND RILEY SCHAEFFER

Received December 10, 1969

The reactions of small carbon molecules generated in a carbon arc with various organic substances have been intensively studied by Skell and coworkers.[1–6] It has also been shown that carbon vapor reacts with

---

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **88,** 3749 (1966).

(2) P. S. Skell and R. R. Engel, *ibid.*, **88,** 4883 (1966).

(3) P. S. Skell and R. R. Engel, *ibid.*, **89,** 2912 (1967).

(4) P. S. Skell and R. F. Harris, *ibid.*, **87,** 5807 (1965).

(5) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89,** 1748 (1967).

(6) P. S. Skell and R. F. Harris, *ibid.*, **91,** 4440 (1969).