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Trigonal Distortion of the CrS_6 Chromophore in Dithiophosphinate Complexes of Chromium(III)

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Abstract

The crystal structures of four compounds of formula $(R_2PS_2)_3Cr$ have been determined from diffractometer data.

I: R = Me, $C2/c$, a = 15.430(3), b = 9.674(2), c = 12.314(1) Å, β = 94.25(1)°, Z = 4, R = 0.030 for 1999 unique observed reflections.

II: R = Ph, $Pbca$, a = 18.191(9), b = 17.748(5), c = 23.487(9) Å, Z = 8, R = 0.044 for 1580 observed unique reflections.

III: R = C_6H_{11}, $P\bar{1}$, a = 9.679(1), b = 11.160(2), c = 20.339(4) Å, α = 91.66(1), β = 103.36(1), γ = 94.74(1)°, Z = 2, R = 0.037 for 4186 unique observed reflections.

IV: R = OEt (redetermined), $C2/c$, a = 14.374(2), b = 13.586(2), c = 14.270(2) Å, β = 90.51(1)°, Z = 4, R = 0.057 for 1535 unique observed reflections.

All four complexes exhibit a trigonal distortion from octahedral symmetry in agreement with both spectroscopic observations and ligand–ligand repulsion calculations. The average distortion in I, II and IV is 12° but in III this is increased to 21°. The additional distortion in III is also manifested in the visible absorption spectrum.

Introduction

Alkyl- and aryl-substituted dithiophosphinate and dithiophosphate complexes of chromium(III), $(R_2PS_2)_3Cr$, have been known for many years [1]. Spectroscopic studies of the CrS_6 chromophore have clearly indicated a lowering of symmetry from O_h to D_3 in these systems [2, 3]. This conclusion is based on the relatively high oscillator strengths of the observed ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ transitions, on the observed splitting of the ${}^4T_{2g}$ and ${}^4T_{1g}(F)$ octahedral states, and on the appropriate selection rules. Most of the studies were carried out in solution where splitting of the states was obtained from a Gaussian analysis of the observed bands [3]. However, for R = OEt, single crystal studies have been carried out in a matrix of the isostructural indium(III) analogue thus allowing a complete analysis including the polarization of the observed transitions [2].

From a consideration of ligand–ligand repulsions, tris(bidentate) complexes have been shown to be susceptible to a trigonal distortion. The amount of distortion of such a complex has been shown to be a function of the ligand bite [4, 5]. With the relatively small bites expected for 1,1-dithiolate ligands, we would qualitatively predict such a distortion to be important in the present case in agreement with the spectroscopic observations.

Until recently, the only structural study on $(R_2PS_2)_3Cr$ compounds was for R = OEt [6]. This structure determination suffered both from a space group ambiguity and from high thermal motion (in other words the structure was poorly defined). The recent report [7] of the structure of the ethyl analogue (R = Et) prompts us to report three new structures of this type, R = Me (I), Ph (II), C_6H_{11} (III) and a redetermination for R = OEt (IV). We are thus able to quantify the distortion observed in the visible spectra and to compare it with predictions from repulsion calculations.

Experimental

All compounds were prepared by literature methods [3]. Dark blue crystals suitable for X-ray analysis for I and IV were obtained by vacuum sublimation, and for II and III from evaporation of $EtOH/CH_2Cl_2$ solutions. Visible absorption spectra were recorded at 21 °C on 0.0017 M solutions in chloroform on a Milton Roy Spectronic 1201 spectrometer.

Crystallography

Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer. Intensities were corrected for absorption and decay. The crystal data, measurement methods, structure solution and refinement are summarized in Table 1. The structures

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TABLE 1. Summary of data collection, structure solution and refinement[a]

	I	II	III	IV
Formula	$C_6H_{18}CrP_3S_6$	$C_{36}H_{30}CrP_3S_6$	$C_{36}H_{66}CrP_3S_6$	$C_{12}H_{30}CrO_6P_3S_6$
Formula weight	427.51	799.94	836.23	607.67
$F(000)$	876	3288	894	1260
Crystal size (mm)	0.30 × 0.20 × 0.15	0.40 × 0.20 × 0.15	0.24 × 0.15 × 0.14	0.30 × 0.15 × 0.10
Space group	$C2/c$	$Pbca$	$P\bar{1}$	$C2/c$
a (Å)	15.430(3)	18.191(9)	9.679(1)	14.374(2)
b (Å)	9.674(2)	17.748(5)	11.160(2)	13.586(2)
c (Å)	12.314(1)	23.487(9)	20.339(4)	14.270(2)
α (°)			91.66(1)	
β (°)	94.25(1)		103.36(1)	90.51(1)
γ (°)			94.74(1)	
V (Å^3)	1833.0	7583.0	2127.5	2786.6
Z	4	8	2	4
ρ (g/cm^3)	1.55	1.40	1.31	1.45
μ (cm^{-1})	15.0	7.6	6.8	10.3
ω scan width (°)	$0.8 + 0.34 \tan \theta$	$0.8 + 0.34 \tan \theta$	$0.7 + 0.34 \tan \theta$	$0.8 + 0.34 \tan \theta$
Maximum 2θ	60.0	54.0	50.0	60.0°
Total reflections	4845	4732	6369	4265
Unique reflections	2668	4103	5845	3504
Decay	0.894 to 1.106	0.858 to 1.101	0.960 to 1.144	0.942 to 1.172
Absorption	0.93 to 1.00	0.90 to 1.00	0.96 to 1.00	0.95 to 1.00
Solution method	Patterson	direct	direct	Patterson
Reflections $F_o^2 > 3\sigma(F_o^2)$	1999	1580	4186	1535
Parameters refined	74	415	415	128
R	0.030	0.044	0.037	0.057
R_w	0.040	0.050	0.047	0.075
GOF	1.24	1.53	1.24	2.21

[a]The following conditions apply to all cases: λ, 0.71073 Å; temperature, 21 ± 1°; graphite crystal monochromator; Zr foil attenuator, factor 19.5; scan type, ω–2θ; scan rate, 1–7°/min in ω; hydrogen atoms refined as riding atoms; function minimized, $\Sigma w(|F_o| - |F_c|)^2$; weights, $4F_o^2/\sigma^2(F_o^2)$.

of **I** and **IV** were solved by Patterson and Fourier methods, and **II** and **III** by direct methods. All four structures were refined on F in full-matrix least-squares with hydrogen atoms included in the model as riding atoms. Scattering factors were taken from Cromer and Waber [8] and anomalous dispersion coefficients were those of Cromer [9]. All calculations were carried out on a VAX 11/750 using VAXSDP [10].

Final atomic parameters are reported in Tables 2–5, and selected derived bond lengths and angles in Tables 6–9. Normal ORTEP [11] plots of the molecules viewed down the approximate threefold axis are given in Figs. 1–4. See also 'Supplementary Material'.

TABLE 2. Positional parameters and their e.s.d.s for I

Atom	x	y	z	B (Å^2)
Cr	0.000	0.17200(5)	0.250	2.489(8)
S1	−0.11187(4)	0.00249(6)	0.28297(4)	3.46(1)
S2	−0.06633(3)	0.16176(6)	0.06494(4)	3.33(1)
S3	0.09032(4)	0.36137(6)	0.19219(6)	3.89(1)
P1	−0.15943(3)	0.05160(6)	0.13115(5)	2.99(1)
P2	0.000	0.48503(9)	0.250	4.20(2)
C1	−0.1892(2)	−0.0998(3)	0.0528(2)	4.92(6)
C2	−0.2583(2)	0.1493(3)	0.1344(3)	4.97(6)
C3	−0.0466(3)	0.5968(4)	0.1454(4)	10.9(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

Results and Discussion

The structures of compounds **I** and **IV** have been solved and reported in the centrosymmetric space group $C2/c$ with the complexes having crystallographic twofold symmetry. Considerable effort was expended to determine whether the high thermal parameters of the light atoms in these structures are due to incorrect assignment of the space group, the non-centrosymmetric group Cc being a possible alternative. We conclude that the compounds are indeed best described in $C2/c$, the high apparent thermal motion not being due to averaged positions from the lower symmetry space group. The thermal

TABLE 3. Positional parameters and their e.s.d.s for II

Atom	x	y	z	B (Å^2)
Cr	0.12402(9)	0.2461(1)	0.12026(7)	5.43(4)
S1	0.0324(2)	0.1499(2)	0.1373(1)	6.07(8)
S2	0.2030(2)	0.1381(2)	0.1055(1)	6.20(8)
S3	0.0362(2)	0.3423(2)	0.1505(1)	7.46(9)
S4	0.1635(1)	0.2553(2)	0.2187(1)	5.60(7)
S5	0.0853(2)	0.2605(2)	0.0216(1)	7.99(9)
S6	0.2221(2)	0.3303(2)	0.0904(1)	6.60(8)
P1	0.1166(2)	0.0769(2)	0.1318(1)	5.28(7)
P2	0.0744(2)	0.3208(2)	0.2284(1)	6.03(8)
P3	0.1709(2)	0.3309(2)	0.0151(1)	6.70(9)
C1	0.0957(5)	0.0008(5)	0.0851(4)	5.4(3)
C2	0.0619(7)	−0.0624(6)	0.1050(4)	8.1(3)
C3	0.0399(6)	−0.1188(6)	0.0674(4)	9.1(4)
C4	0.0507(7)	−0.1121(7)	0.0113(4)	9.1(4)
C5	0.0857(8)	−0.0499(7)	−0.0090(5)	12.2(5)
C6	0.1083(7)	0.0074(7)	0.0293(4)	9.4(4)
C7	0.1345(5)	0.0331(6)	0.1983(4)	5.3(3)
C8	0.0924(6)	0.0455(6)	0.2456(4)	6.5(3)
C9	0.1071(7)	0.0094(6)	0.2977(4)	8.7(4)
C10	0.1657(6)	−0.0395(7)	0.3016(5)	8.4(3)
C11	0.2076(6)	−0.0536(6)	0.2541(5)	8.1(3)
C12	0.1919(6)	−0.0176(7)	0.2035(4)	7.6(4)
C13	0.0061(5)	0.2767(5)	0.2717(4)	5.1(3)
C14	0.0242(6)	0.2176(7)	0.3071(4)	7.9(4)
C15	−0.0293(7)	0.1856(7)	0.3420(5)	10.6(4)
C16	−0.1017(6)	0.2091(7)	0.3407(5)	9.8(4)
C17	−0.1182(6)	0.2679(7)	0.3046(5)	9.0(4)
C18	−0.0668(5)	0.3008(6)	0.2705(4)	6.9(3)
C19	0.0969(5)	0.4076(6)	0.2662(5)	7.0(3)
C20	0.1162(8)	0.3965(8)	0.3240(5)	12.6(5)
C21	0.1398(8)	0.4649(8)	0.3559(5)	13.9(5)
C22	0.1318(8)	0.5292(7)	0.3208(7)	16.0(6)
C23	0.1173(7)	0.5466(8)	0.2714(8)	17.3(6)
C24	0.0993(7)	0.4733(6)	0.2434(8)	14.3(5)
C25	0.1412(6)	0.4246(6)	−0.0041(4)	7.3(3)
C26	0.1816(7)	0.4855(7)	0.0097(6)	12.6(5)
C27	0.1611(8)	0.5588(8)	−0.0059(6)	15.8(5)
C28	0.1026(9)	0.5685(8)	−0.0365(6)	14.9(6)
C29	0.0602(7)	0.5107(7)	−0.0526(5)	10.8(4)
C30	0.0779(7)	0.4362(7)	−0.0357(5)	9.9(4)
C31	0.2303(6)	0.2998(8)	−0.0418(4)	8.7(4)
C32	0.3029(8)	0.2805(8)	−0.0340(6)	12.7(5)
C33	0.3460(9)	0.2562(8)	−0.0824(6)	15.3(5)
C34	0.3204(9)	0.2605(8)	−0.1340(5)	13.5(5)
C35	0.2535(8)	0.288(1)	−0.1388(6)	23.3(9)
C36	0.2120(7)	0.308(1)	−0.0934(5)	21.6(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

parameters in **II** are also high but there is no space group ambiguity here. In this case we attempted to find a disorder model to account for this effect. Refinement of disorder models did not improve the fit, hence we report the results of the refinements of the ordered model.

TABLE 4. Positional parameters and their e.s.d.s for III

Atom	x	y	z	B (Å^2)
Cr	0.51019(6)	0.49455(5)	0.24858(3)	2.50(1)
S1	0.5526(1)	0.71458(8)	0.26332(5)	3.05(2)
S2	0.2629(1)	0.54427(9)	0.21154(5)	3.18(2)
S3	0.5528(1)	0.48302(9)	0.37208(5)	3.08(2)
S4	0.4185(1)	0.28468(9)	0.25341(5)	3.38(2)
S5	0.5097(1)	0.45221(9)	0.12972(5)	3.15(2)
S6	0.7663(1)	0.48875(9)	0.26141(5)	3.07(2)
P1	0.3401(1)	0.71814(9)	0.23150(5)	2.76(2)
P2	0.4644(1)	0.31194(9)	0.35495(5)	2.95(2)
P3	0.7231(1)	0.45139(9)	0.16061(5)	2.74(2)
C1	0.2974(4)	0.8086(3)	0.1570(2)	3.15(8)
C2	0.3648(5)	0.7640(4)	0.1015(2)	4.4(1)
C3	0.3277(5)	0.8386(4)	0.0386(2)	5.1(1)
C4	0.3674(5)	0.9709(4)	0.0556(2)	5.3(1)
C5	0.3011(5)	1.0154(4)	0.1111(2)	5.0(1)
C6	0.3391(5)	0.9426(3)	0.1742(2)	4.1(1)
C7	0.2574(4)	0.7861(3)	0.2941(2)	3.13(8)
C8	0.0975(4)	0.7906(4)	0.2667(2)	4.8(1)
C9	0.0281(5)	0.8441(5)	0.3192(2)	6.3(1)
C10	0.0574(5)	0.7765(5)	0.3838(2)	6.2(1)
C11	0.2148(5)	0.7726(4)	0.4117(2)	4.9(1)
C12	0.2855(4)	0.7191(4)	0.3594(2)	3.9(1)
C13	0.5817(4)	0.2008(3)	0.3949(2)	3.29(9)
C14	0.5055(5)	0.0729(3)	0.3820(2)	4.5(1)
C15	0.6031(5)	−0.0190(4)	0.4142(2)	5.3(1)
C16	0.7399(5)	−0.0115(4)	0.3900(3)	5.8(1)
C17	0.8167(5)	0.1117(4)	0.4029(3)	5.4(1)
C18	0.7208(4)	0.2075(4)	0.3718(2)	4.7(1)
C19	0.3084(4)	0.2926(4)	0.3908(2)	3.43(9)
C20	0.2053(5)	0.3853(4)	0.3651(2)	5.4(1)
C21	0.0738(5)	0.3740(5)	0.3953(2)	6.2(1)
C22	0.1151(5)	0.3788(5)	0.4713(3)	6.6(1)
C23	0.2168(5)	0.2868(4)	0.4971(2)	4.9(1)
C24	0.3480(4)	0.2991(4)	0.4682(2)	4.0(1)
C25	0.7884(4)	0.3069(3)	0.1442(2)	3.10(8)
C26	0.9500(5)	0.3131(4)	0.1671(2)	4.7(1)
C27	1.0055(5)	0.1918(4)	0.1557(3)	6.0(1)
C28	0.9353(6)	0.0933(4)	0.1898(3)	6.3(1)
C29	0.7748(5)	0.0856(4)	0.1646(3)	5.6(1)
C30	0.7157(5)	0.2050(4)	0.1756(2)	5.1(1)
C31	0.8129(4)	0.5611(3)	0.1150(2)	3.03(8)
C32	0.7888(5)	0.5215(4)	0.0404(2)	4.1(1)
C33	0.8602(5)	0.6138(4)	0.0023(2)	5.1(1)
C34	0.8103(5)	0.7370(4)	0.0097(2)	5.3(1)
C35	0.8347(5)	0.7769(4)	0.0829(2)	4.4(1)
C36	0.7649(4)	0.6868(3)	0.1226(2)	3.78(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

The coordination sphere of chromium is qualitatively the same in all four cases. As seen from Tables 6–9, the Cr–S bond lengths range from 2.419 to 2.459 Å, those of the cyclohexyl derivative being slightly longer than the others. The angles subtended by the ligands at chromium (S–Cr–S) are all similar (81.13–82.79°), as are the angles at sulfur (Cr–S–P, 84.29–87.18°). The phosphorus atoms are tetrahedral, the S–P–S angle being close to ideal in all cases.

TABLE 5. Positional parameters and their e.s.d.s for **IV**

Atom	x	y	z	B (Å^2)
Cr	1.000	0.18139(9)	0.750	5.27(3)
S1	0.9176(1)	0.1657(1)	0.6019(1)	7.08(4)
S2	0.8849(1)	0.0620(1)	0.7999(1)	7.34(4)
S3	0.9090(1)	0.3155(1)	0.8140(1)	7.02(4)
P1	0.8343(1)	0.0735(1)	0.6694(1)	7.43(4)
P2	1.000	0.4039(2)	0.750	7.05(6)
O1	0.8198(3)	−0.0281(3)	0.6193(4)	8.8(1)
O2	0.7285(3)	0.1045(4)	0.6623(4)	10.7(2)
O3	0.9526(3)	0.4815(3)	0.6839(3)	8.7(1)
C1	0.8977(5)	−0.0895(5)	0.5963(6)	10.1(2)
C2	0.8622(5)	−0.1817(5)	0.5571(5)	8.9(2)
C3	0.6972(7)	0.2000(7)	0.685(1)	16.1(4)
C4	0.6093(7)	0.2225(8)	0.6572(8)	15.1(3)
C5	0.8843(6)	0.4500(5)	0.6130(6)	11.3(2)
C6	0.8595(6)	0.5317(6)	0.5554(7)	12.5(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

The deviation from octahedral symmetry has been evaluated from the trigonal twist angle (60° for an undistorted octahedron). These are calculated as the three S–m–m′–S′ torsion angles, where m and m′ are the centers of the appropriate trianglular faces, and then averaged. The values obtained are 49.2, 48.0, 38.8 and 47.4° for **I**, **II**, **III** and **IV** respectively. The equivalent angle reported for the ethyl substituted analogue [7] is 47.2°. It is seen that the trigonal twists for the compounds with small substituents or phenyl groups are all clustered around 48°. The values are within a few degrees of those predicted by the equations of Avdeef and Fackler [5] for the ligand bites observed (1.30–1.32). The cyclohexyl analogue is anomalous in this respect. Not only does it have a trigonal distortion almost double that observed for the other compounds, but the calculated twist angle is also 11° smaller than predicted from ligand–ligand repulsion calculations [5]. In other words, the coordination polyhedron is 11° further away from octahedral symmetry than expected.

TABLE 6. Bond distances (Å) and angles (°) in **I** with e.s.d.s in parentheses

Distances							
Cr	S1	2.4366(7)		S3	P2	2.0068(8)	
Cr	S2	2.4299(5)		P1	C1	1.795(3)	
Cr	S3	2.4398(7)		P1	C2	1.797(3)	
S1	P1	2.0138(8)		P2	C3	1.791(4)	
S2	P1	2.0096(8)					
Angles							
S1	Cr	S1′	95.41(3)	Cr	S3	P2	85.26(3)
S1	Cr	S2	82.79(2)	S1	P1	S2	106.22(3)
S1	Cr	S2′	94.05(2)	S1	P1	C1	111.56(9)
S1	Cr	S3	168.81(2)	S1	P1	C2	110.8(1)
S1	Cr	S3′	91.70(2)	S2	P1	C1	112.1(1)
S2	Cr	S2′	175.33(3)	S2	P1	C2	111.3(1)
S2	Cr	S3	88.11(2)	C1	P1	C2	104.9(1)
S2	Cr	S3′	95.41(2)	S3	P2	S3′	106.82(5)
S3	Cr	S3	82.67(2)	S3	P2	C3	110.9(1)
Cr	S1	P1	84.29(3)	S3	P2	C3′	111.3(1)
Cr	S2	P1	84.56(3)	C3	P2	C3′	105.7(2)

TABLE 7. Selected bond distances (Å) and angles (°) in **II** with e.s.d.s in parentheses

Distances					
Cr	S1	2.419(3)	S4	P2	2.008(4)
Cr	S2	2.421(3)	S5	P3	2.002(5)
Cr	S3	2.444(4)	S6	P3	2.001(4)
Cr	S4	2.426(3)	P1	C1	1.781(9)
Cr	S5	2.436(3)	P1	C7	1.775(9)
Cr	S6	2.431(3)	P2	C13	1.79(1)
S1	P1	2.010(4)	P2	C19	1.83(1)
S2	P1	2.007(4)	P3	C25	1.80(1)
S3	P2	1.996(4)	P3	C31	1.81(1)

(continued)

TABLE 7. *(continued)*

Angles							
S1	Cr	S2	82.7(1)	Cr	S6	P3	85.2(1)
S1	Cr	S3	89.7(1)	S1	P1	S2	105.5(1)
S1	Cr	S4	95.4(1)	S1	P1	C1	111.4(3)
S1	Cr	S5	91.9(1)	S1	P1	C7	111.4(3)
S1	Cr	S6	170.8(1)	S2	P1	C1	112.8(4)
S2	Cr	S3	169.4(1)	S2	P1	C7	111.4(4)
S2	Cr	S4	90.8(2)	C1	P1	C7	104.5(4)
S2	Cr	S5	96.8(2)	S3	P2	S4	106.7(2)
S2	Cr	S6	90.6(2)	S3	P2	C13	111.4(4)
S3	Cr	S4	82.5(1)	S3	P2	C19	111.3(4)
S3	Cr	S5	90.8(1)	S4	P2	C13	111.9(3)
S3	Cr	S6	97.7(1)	S4	P2	C19	111.3(3)
S4	Cr	S5	170.1(1)	C13	P2	C19	104.4(5)
S4	Cr	S6	90.9(2)	S5	P3	S6	106.9(1)
S5	Cr	S6	82.7(1)	S5	P3	C25	111.2(4)
Cr	S1	P1	85.4(1)	S5	P3	C31	109.3(5)
Cr	S2	P1	85.4(1)	S6	P3	C25	111.4(4)
Cr	S3	P2	84.5(1)	S6	P3	C31	111.9(4)
Cr	S4	P2	84.8(1)	C25	P3	C31	106.1(5)
Cr	S5	P3	85.0(2)				

TABLE 8. Selected bond distances (Å) and angles (°) in III with e.s.d.s in parentheses

Distances							
Cr	S1	2.454(1)		S4	P2	2.018(1)	
Cr	S2	2.452(1)		S5	P3	2.016(1)	
Cr	S3	2.459(1)		S6	P3	2.019(1)	
Cr	S4	2.448(1)		P1	C1	1.832(4)	
Cr	S5	2.449(1)		P1	C7	1.830(4)	
Cr	S6	2.439(1)		P2	C13	1.831(4)	
S1	P1	2.013(1)		P2	C19	1.823(5)	
S2	P1	2.016(1)		P3	C25	1.830(4)	
S3	P2	2.013(1)		P3	C31	1.838(4)	
Angles							
S1	Cr	S2	81.34(4)	Cr	S6	P3	86.93(5)
S1	Cr	S3	89.21(4)	S1	P1	S2	105.06(6)
S1	Cr	S4	163.53(5)	S1	P1	C1	110.4(1)
S1	Cr	S5	104.10(4)	S1	P1	C7	113.7(1)
S1	Cr	S6	87.87(4)	S2	P1	C1	112.5(1)
S2	Cr	S3	105.17(4)	S2	P1	C7	109.7(1)
S2	Cr	S4	88.32(4)	C1	P1	C7	105.6(2)
S2	Cr	S5	88.39(4)	S3	P2	S4	104.66(6)
S2	Cr	S6	163.10(4)	S3	P2	C13	113.8(1)
S3	Cr	S4	81.13(4)	S3	P2	C19	110.0(1)
S3	Cr	S5	162.42(4)	S4	P2	C13	110.0(1)
S3	Cr	S6	87.54(4)	S4	P2	C19	113.5(1)
S4	Cr	S5	88.28(4)	C13	P2	C19	105.0(2)
S4	Cr	S6	104.89(4)	S5	P3	S6	104.68(6)
S5	Cr	S6	81.64(4)	S5	P3	C25	113.7(1)
Cr	S1	P1	86.80(4)	S5	P3	C31	110.3(1)
Cr	S2	P1	86.79(5)	S6	P3	C25	109.4(1)
Cr	S3	P2	86.99(4)	S6	P3	C31	113.5(1)
Cr	S4	P2	87.18(4)	C25	P3	C31	105.4(2)
Cr	S5	P3	86.73(4)				

TABLE 9. Selected bond distances (Å) and angles (°) in IV with e.s.d.s in parentheses

Distances					
Cr	S1	2.423(2)	S3	P2	2.002(2)
Cr	S2	2.428(2)	P1	O1	1.569(5)
Cr	S3	2.426(2)	P1	O2	1.581(5)
S1	P1	1.988(3)	P2	O3	1.566(5)
S2	P1	1.999(3)			

Angles							
S1	Cr	S1′	169.93(8)	Cr	S3	P2	85.52(8)
S1	Cr	S2	82.42(6)	S1	P1	S2	106.6(1)
S1	Cr	S2′	90.85(6)	S1	P1	O1	114.3(2)
S1	Cr	S3	97.66(6)	S1	P1	O2	112.6(2)
S1	Cr	S3′	89.91(6)	S2	P1	O1	113.7(2)
S2	Cr	S2′	96.22(7)	S2	P1	O2	115.0(3)
S2	Cr	S3	91.12(6)	O1	P1	O2	94.7(3)
S2	Cr	S3′	169.44(6)	S3	P2	S3′	106.3(1)
S3	Cr	S3′	82.68(7)	S3	P2	O3	113.3(2)
Cr	S1	P1	85.67(8)	S3	P2	O3′	114.3(2)
Cr	S2	P1	85.26(8)	O3	P2	O3′	95.4(3)

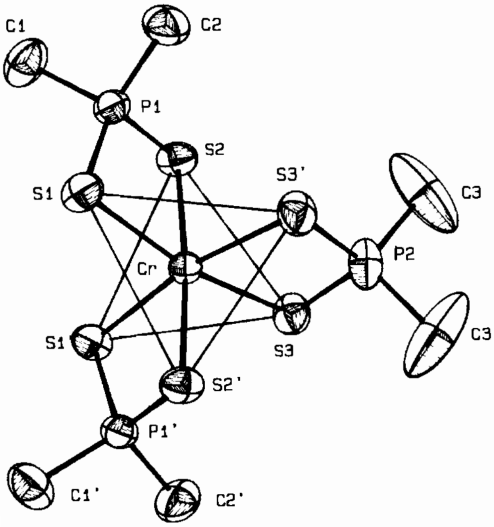

Fig. 1. Molecule I viewed down the pseudo-trigonal axis.

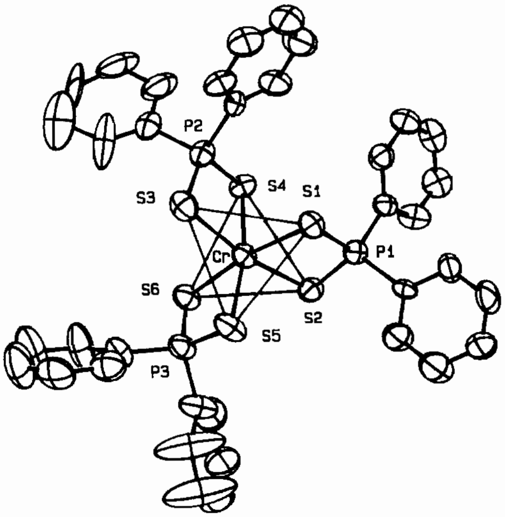

Fig. 2. Molecule II viewed down the pseudo-trigonal axis.

We have previously observed this anomaly with complexes of this ligand with the tervalent lanthanide ions [12]. It is tempting to ascribe the additional distortion to interactions between cyclohexyl groups on neighboring ligands, however, there are no close contacts observed to support this argument. We note, however, that as the minimum in the repulsion energy moves further away from octahedral, it also becomes more shallow, especially with respect to the energy at the trigonal prismatic limit [5]. Thus any additional steric effects beyond the CrS_6 core that favor further trigonal distortion would be accentuated at lower twist angles.

We have thus demonstrated that a trigonal distortion of 12° form O_h is sufficient to generate the effects seen in the visible absorption spectra. However, having observed that the trigonal distortion for **III** is almost double that for the other three compounds reported here, or for the ethyl analogue, we would expect this to also be observable in the visible absorption spectrum. In Fig. 5 we show the visible spectrum of **III** superimposed on that of **IV**. It is clear that the low energy $^4T_{2g} \leftarrow {}^4A_{2g}$ band (O_h) is considerably broader for **III**, and is now resolved into a doublet even in solution and at room temperature. The effect on the high energy $^4T_{1g} \leftarrow {}^4A_{2g}$ transition is much less. This is in agreement with analysis of the spectrum in D_3 symmetry. Both the $^4E \leftarrow {}^4A_2$ and $^4E \leftarrow {}^4A_2$ (derived from $^4T_{2g} \leftarrow {}^4A_{2g}$) are allowed electric-dipole transitions,

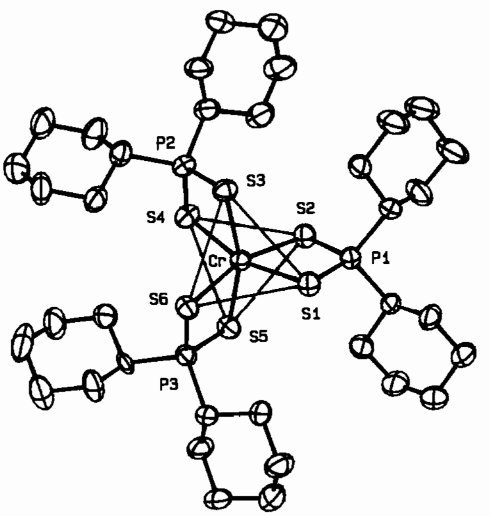

Fig. 3. Molecule III viewed down the pseudo-trigonal axis.

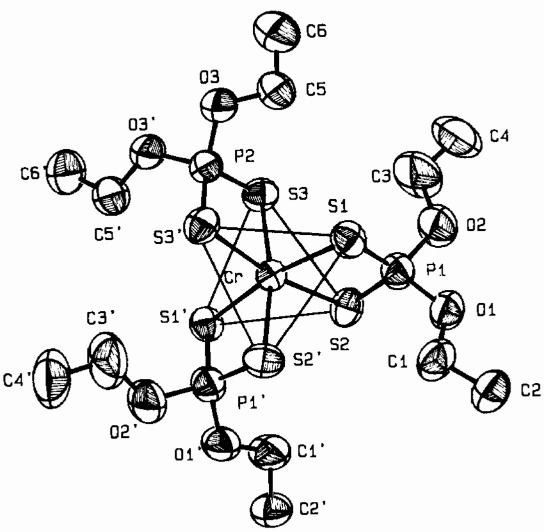

Fig. 4. Molecule IV viewed down the pseudo-trigonal axis.

but only the $^4E \leftarrow {}^4A_2$ component of the split $^4T_{1g}$ level is electric-dipole allowed. The doubling of the high energy band in IV has been previously assigned to observation of a spin forbidden component ($^2T_{2g} \leftarrow {}^4A_{2g}$ in O_h symmetry).

In conclusion, we confirm that the spectral properties previously observed for these molecules are due to a trigonal distortion from O_h symmetry and quantify the distortion at ~12°. Although this distortion is enough to give significant intensity to the formally forbidden bands, the splitting of the levels may not be observed in solution. However, when the distortion is doubled (compound III), then the two components of the $^4T_{2g} \leftarrow {}^4A_{2g}$ band may be resolved in solution.

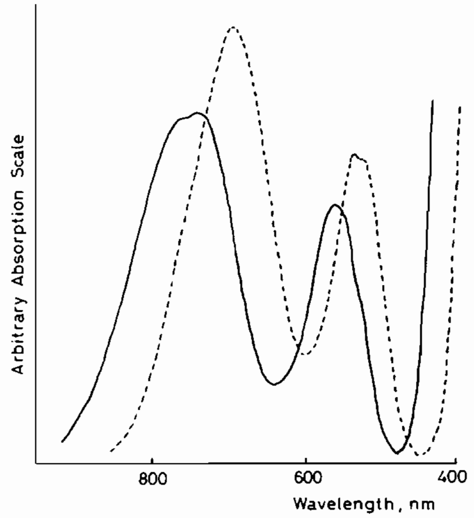

Fig. 5. Visible absorption spectrum of III (——) and IV (-------).

Supplementary Material

A complete structure report including tables of observed and calculated structure factors, anisotropic temperature factors, calculated hydrogen positions and tables of bond lengths and angles is available on request.

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