CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIS(1,10-PHENANTHROLINE)POTASSIUM SALT OF μ-HYDRIDOBIS[PENTACARBONYLCHROMIUM(0)]

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Summary

The crystal and molecular structure of $[K(phen)_3][Cr_2(CO)_{10}(\mu\text{-H})]$ has been determined by X-ray diffraction. The compound crystallizes in the space group $P\bar{1}$ with a 11.884(4), b 13.968(4), c 15.612(6) Å, α 112.6(1), β 99.7(1) and γ 106.2(1)° and $Z = 2$. The structure was refined to $R = 0.066$ and $R_w = 0.067$ for 3692 counter data with $I \geqslant 3\sigma(I)$.

The complex anion $[Cr_2(CO)_{10}(\mu\text{-H})]$ adopts a bent Cr–H–Cr configuration with the equatorial carbonyl groups of the two independent $Cr(CO)_5$ moieties in an eclipsed configuration. The Cr $\cdots$ Cr distance is 3.394(3) Å and the two Cr–H bonds are 1.74(7) and 1.71(7) Å. The Cr–H–Cr bond angle is 159(3)°. In the dimeric complex cation $[K(phen)_3]_2$, located on inversion center, the coordination polyhedron around K is unexpectedly cubic; the particular disposition of the phen molecules with short intermolecular contacts (minimum value 3.38 Å) could stabilize this otherwise unfavourable cubic geometry. The K $\cdots$ K' separation is 4.15 Å and the K–N bond distances range from 2.835(6) to 3.117(7) Å for the non-bridging nitrogens and from 2.907(6) to 3.342(6) Å for the bridging nitrogens.

Introduction

The title compound was recently obtained as the most stable product of the reaction of $K[Cr_2H(CO)_{10}]$ with 1,10-phenanthroline (phen). The question arose of whether it contained the previously unknown $[K(phen)_3]^+$ cation or instead involved

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a donor–acceptor interaction between one phen molecule and the Cr–H–Cr electron-deficient system of the complex anion [1]. IR and Raman investigations gave only indirect indication of the presence of a $[K(phen)_3]^+$ cation [2]. Recently, however, clear evidence for the existence of the species $[K(phen)_3]_2^{2+}$ has been obtained with the isolation of the $[K(phen)_3][BPh_4]$ compound [3] and demonstration by X-ray diffraction that it involves dimeric $[K(phen)_3]_2^{2+}$ cations with the potassium ion 8-coordinated to the nitrogens of the phen ligands in a square antiprismatic geometry [4]. It was thus of interest to determine the structure of the title compound in order to determine the nature of its complex cation and the extent to which packing effects and cation–anion interactions might influence the structure of the cation and the anion.

Experimental

The compound was prepared by a published procedure [1].

Crystal data. $KCr_2C_{46}O_{10}N_6H_{25}$. Mol.wt. 964.7, triclinic $P\bar{1}$. The unit cell dimensions are: a 11.884(4), b 13.968(4), c 15.612(6) Å, α 112.6(1), β 99.7(1), γ, 106.2(1)°, U 2183.2 Å^3, $Z = 2$ and $D_c = 1.47$ Mg m^{-3}, λ (Mo-K_α) 0.7107 Å.

Crystal habit: white prism of dimensions $0.2 \times 0.3 \times 0.2$ mm. Reflections data were collected at room temperature in the scan range $2\theta = 3$–$50°$ on a Siemens Stoe four-circle diffractometer, using graphite monochromatized Mo-K_α radiation and employing the ω–θ scan techniques, with a 0.5 s count at each of 120 steps of $0.01°$ for each reflection and a 10 s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of attenuators into the beam. Two standard reflections, $3\,\bar{1}\,4$ and $3\,2\,4$, measured after approximately 150 data reflections, showed only random fluctuations. Of the 6380 measured independent reflections, 3692 with $I \geqslant 3\sigma(I)$ were used for solution and refinement of the structure. Intensities were corrected for Lorentz and polarization effects and converted to an absolute scale by Wilson's method.

The structure was solved by direct methods [5] and refined by a full-matrix least-squares procedure. The function $\Sigma w \|F_0| - |F_c\|^2$ was minimized, in which $w = 2.9542 \, |\sigma^2(F_0) + 8.6 10^{-4}(F_0)^2|^{-1}$ in the last refinement cycles.

Because of the large number of parameters, 585 with anisotropic thermal parameters for all non-hydrogen atoms, the structure was refined in blocks of 212 and 284 parameters refining alternately the heavy atoms (Cr(1), Cr(2) and K) with the carbonyl ligands and with the phen molecules according to the following sequence:
1 block: Cr(1)–Cr(2) K, 10 carbonyls
2 block: Cr(1)–Cr(2) K, phen(1), phen(3)
3 block: Cr(1)–Cr(2) K, 10 carbonyls
4 block: Cr(1), Cr(2) K, phen(2), phen(3)
5 block: Cr(1), Cr(2) K, 10 carbonyls
6 block: Cr(1), Cr(2) K, phen(1), phen(2)

At this point, at a R value of 0.073, a Fourier difference synthesis showed electron density residuals of the order of 0.8 e Å^{-3} near the phenanthroline carbon atoms and a larger residual of about 1.5 e Å^{-3} between the chromium atoms, these being interpreted as due to hydrogen atom positions. The H belonging to the phenanthrolines were introduced at ideal calculated positions (C–H 0.95 Å) with isotropic $U = 0.08$ Å^2, and the hydridic hydrogen was introduced at the found position and

TABLE 1

FRACTIONAL COORDINATES ($\times 10^4$) FOR NONHYDROGEN ATOMS AND THE HYDRIDIC HYDROGEN WITH e.s.d.'s IN PARENTHESES

Atom	x	y	z	Atom	x	y	z
Cr(1)	7298(1)	1032(1)	−825(1)	C(46)	5808(7)	4245(7)	5374(7)
Cr(2)	5562(1)	2620(1)	9371(1)	N(1)	10035(5)	4803(4)	6380(4)
K	11229(1)	4187(1)	4886(1)	N(2)	8556(5)	3191(4)	4546(4)
O(1)	8166(6)	1720(4)	1336(4)	C(11)	10771(7)	5521(6)	7261(6)
O(2)	5009(6)	−878(5)	−1153(4)	C(12)	10564(7)	5534(6)	8114(5)
O(3)	6583(5)	250(5)	−3008(4)	C(13)	9526(7)	4736(6)	8035(5)
O(4)	9509(6)	2964(6)	−546(4)	C(14)	8715(6)	3947(5)	7129(5)
O(5)	8675(8)	−484(6)	−1119(5)	C(15)	7629(7)	3087(6)	6981(5)
O(6)	6168(6)	3629(6)	1571(4)	C(16)	6883(7)	2303(6)	6094(6)
O(7)	7748(6)	4589(5)	9648(4)	C(17)	7162(6)	2314(5)	5226(5)
O(8)	4803(5)	1576(5)	7169(4)	C(18)	6433(7)	1509(6)	4310(6)
O(9)	3406(6)	739(6)	9232(5)	C(19)	6771(8)	1531(7)	3521(5)
O(10)	3884(7)	3834(6)	−741(6)	C(20)	7826(8)	2385(7)	3674(5)
C(1)	7813(7)	1460(6)	528(5)	C(21)	8226(6)	3149(5)	5332(4)
C(2)	5864(8)	−139(7)	−1008(5)	C(22)	9001(6)	3982(5)	6286(5)
C(3)	6834(7)	581(6)	−2174(5)	N(3)	11209(6)	2830(5)	6073(5)
C(4)	8666(8)	2193(7)	−660(5)	N(4)	10545(6)	1775(5)	4078(5)
C(5)	8144(9)	106(7)	−1000(6)	C(23)	11544(7)	3304(7)	7049(7)
C(6)	5962(7)	3244(6)	736(6)	C(24)	10926(9)	2863(8)	7586(6)
C(7)	6931(8)	3841(7)	9537(5)	C(25)	9923(9)	1913(7)	7083(7)
C(8)	5134(7)	1955(6)	7994(6)	C(26)	9518(7)	1367(7)	6057(6)
C(9)	4242(8)	1467(7)	9281(6)	C(27)	8470(8)	352(7)	5500(7)
C(10)	4539(8)	3367(7)	−679(6)	C(28)	8135(7)	−166(6)	4529(7)
N(5)	6313(6)	4367(5)	4673(5)	C(29)	8828(7)	298(6)	4016(6)
N(6)	7615(7)	5786(6)	6624(5)	C(30)	8514(8)	−242(7)	2997(7)
C(35)	5651(10)	3663(9)	3743(7)	C(31)	9212(9)	217(8)	2541(6)
C(36)	4471(12)	2853(9)	3468(10)	C(32)	10209(8)	1208(8)	3106(7)
C(37)	3978(11)	2759(10)	4165(15)	C(33)	9852(6)	1313(6)	4540(5)
C(38)	4626(9)	3473(9)	5129(10)	C(34)	10197(7)	1861(6)	5578(6)
C(39)	4143(13)	3408(12)	5886(14)	H	6601(57)	2007(48)	−515(42)
C(40)	4725(15)	4015(15)	6795(13)				
C(41)	5927(11)	4889(9)	7095(9)				
C(42)	6585(17)	5630(15)	8037(12)				
C(43)	7711(15)	6418(13)	8288(8)				
C(44)	8202(9)	6476(8)	7549(8)				
C(45)	6459(8)	4971(7)	6351(7)				

refined isotropically. The final model in the space group $P\bar{1}$ reached convergence with $R = 0.066$ and R_w 0.067 for the 3692 observed reflections. Final coordinates for nonhydrogen atoms are in Table 1. Bond lengths and valence angles are given in Tables 2–4. Intermolecular contacts are in Table 5. The calculations were carried out on the IBM 4331 computer of the University of Messina, with the SHELX-76 program for crystal structure [6] *.

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* Thermal parameters, hydrogen atom coordinates, and structure factor tables are available on request from the authors.

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH e.s.d 's IN PARENTHESES FOR THE
$[Cr_2(CO)_{10}(\mu\text{-H})]^-$ ANION

Cr(1)–H	1.74(7)	Cr(2)–H	1.71(7)
Cr(1)–C(1)	1.893(8)	Cr(2)–C(6)	1.878(8)
Cr(1)–C(2)	1.892(9)	Cr(2)–C(7)	1.895(8)
Cr(1)–C(3)	1.880(8)	Cr(2)–C(8)	1.891(8)
Cr(1)–C(4)	1.845(9)	Cr(2)–C(9)	1.847(9)
Cr(1)–C(5)$_{ax}$	1.818(12)	Cr(2)–C(10)$_{ax}$	1.820(11)
Cr $\cdots$ Cr′	3.395		
C(1)–O(1)	1.133(10)	C(6)–O(6)	1.152(10)
C(2)–O(2)	1.143(10)	C(7)–O(7)	1.141(10)
C(3)–O(3)	1.152(10)	C(8)–O(8)	1.133(10)
C(4)–O(4)	1.178(11)	C(9)–O(9)	1.173(11)
C(5)–O(5)	1.151(15)	C(10)–O(10)	1.161(15)
C(4)–Cr(1)–C(5)	91.2(5)	Cr(1)–C(1)–O(1)	177.3(8)
C(3)–Cr(1)–C(5)	89.5(4)	Cr(1)–C(2)–O(2)	176.9(7)
C(3)–Cr(1)–C(4)	89.2(4)	Cr(1)–C(3)–O(3)	175.4(8)
C(2)–Cr(1)–C(5)	90.3(4)	Cr(1)–C(4)–O(4)	177.0(9)
C(2)–Cr(1)–C(4)	178.2(4)	Cr(1)–C(5)–O(5)	179.4(8)
C(2)–Cr(1)–C(3)	90.1(3)	Cr(2)–C(6)–O(6)	177.6(8)
C(1)–Cr(1)–C(5)	88.3(4)	Cr(2)–C(7)–O(7)	178.8(7)
C(1)–Cr(1)–C(4)	90.3(4)	Cr(2)–C(8)–O(8)	175.0(8)
C(1)–Cr(1)–C(3)	177.7(4)	Cr(2)–C(9)–O(9)	179.4(7)
C(1)–Cr(1)–C(2)	90.5(4)	Cr(2)–C(10)–O(10)	177.9(8)
C(9)–Cr(2)–C(10)	88.2(4)	C(1)–Cr(1)–H	85(2)
C(8)–Cr(2)–C(10)	89.4(4)	C(2)–Cr(1)–H	92(2)
C(8)–Cr(2)–C(9)	90.0(4)	C(3)–Cr(1)–H	97(2)
C(7)–Cr(2)–C(10)	91.6(4)	C(4)–Cr(1)–H	86(2)
C(7)–Cr(2)–C(9)	176.9(3)	C(5)–Cr(1)–H	173(2)
C(7)–Cr(2)–C(8)	93.1(3)	C(6)–Cr(2)–H	86(2)
C(6)–Cr(2)–C(10)	91.0(4)	C(7)–Cr(2)–H	85(2)
C(6)–Cr(2)–C(9)	88.6(4)	C(8)–Cr(2)–H	93(2)
C(6)–Cr(2)–C(8)	178.5(4)	C(9)–Cr(2)–H	95(2)
C(6)–Cr(2)–C(7)	88.4(4)	C(10)–Cr(2)–H	176(2)

Atomic scattering factors were taken from ref. 7 and anomalous dispersion terms
[7] for Cr were included in F_c calculations.

Results and discussion

The crystal and molecular structure of $[K(phen)_3][Cr_2H(CO)_{10}]$ is shown in Fig.
1. It consists of $[Cr_2(CO)_{10}(\mu\text{-H})]^-$ anions and $[K(phen)_3]^+$ cations. Close examina-
tion of the intermolecular contacts excludes direct interaction between phen mole-
cules and the complex anion, which shows a "bent eclipsed" geometry.

The complex cation is a dimer, as in $[K(phen)_3][BPh_4]$ [4], and the dimeric units
are located on the crystallographic inversion centres; this prevents any arrangement
of the complex anion at these centres.

The dimers consist of double centrosymmetric bridges involving two phen mole-
cules, each N atom of which is shared between two K atoms with a K $\cdots$ K′

TABLE 3

POTASSIUM COORDINATION SPHERE[a]

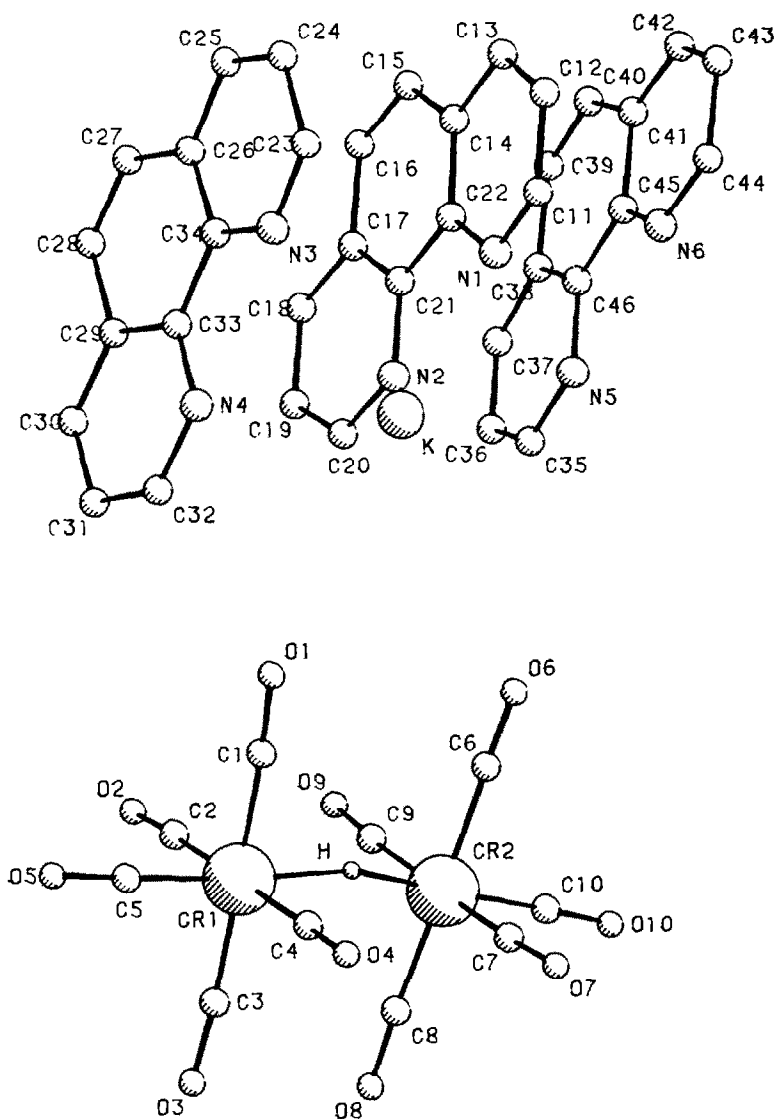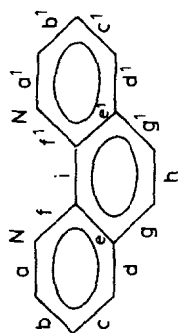| (a) Distances (Å)		(b) Angles (°)	
K...K'	4.156	N(1)–K–N(2)	52.9(2)
K–N(1)	2.907(6)	N(3)–K–N(4)	53.9(2)
K–N(2)	2.950(6)	N(5)–K–N(6)	57.4(2)
K–N(3)	3.117(7)	N'(1)–K–N'(2)	49.3(2)
K–N(4)	2.908(6)		
K–N(5)	2.835(6)		
K–N(6)	2.929(6)		
K–N'(1)	3.239(6)		
K–N'(2)	3.342(6)		

[a] Primed atoms are centrosymmetrically related to the unprimed.

Fig. 1. View down a of the [K(phen)$_3$][Cr$_2$(CO)$_{10}$-μ-H] structure.

TABLE 4

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES FOR THE PHEN MOLECULES

(a) Distances

	phen 1		phen 2		phen 3	
a	N(2)–C(20)	1.324(7)	N(3)–C(23)	1.338(12)	N(5)–C(35)	1.333(11)
a₁	N(1)–C(11)	1.307(8)	N(4)–C(32)	1.336(12)	N(6)–C(44)	1.310(11)
b	C(19)–C(20)	1.378(11)	C(23)–C(24)	1.405(16)	C(35)–C(36)	1.403(15)
b₁	C(11)–C(12)	1.388(13)	C(31)–C(32)	1.375(11)	C(43)–C(44)	1.396(21)
c	C(18)–C(19)	1.366(14)	C(24)–C(25)	1.341(11)	C(36)–C(37)	1.351(28)
c₁	C(12)–C(13)	1.361(11)	C(30)–C(31)	1.362(16)	C(42)–C(43)	1.350(23)
d	C(17)–C(18)	1.364(8)	C(25)–C(26)	1.405(13)	C(37)–C(38)	1.371(20)
d₁	C(13)–C(14)	1.376(8)	C(29)–C(30)	1.401(12)	C(41)–C(42)	1.355(17)
e	C(17)–C(21)	1.394(9)	C(26)–C(34)	1.407(14)	C(38)–C(46)	1.392(13)
e₁	C(14)–C(22)	1.429(11)	C(29)–C(33)	1.404(8)	C(41)–C(45)	1.439(19)
f	N(2)–C(21)	1.367(10)	N(3)–C(34)	1.360(8)	N(5)–C(46)	1.377(14)
f₁	N(1)–C(22)	1.366(8)	N(4)–C(33)	1.370(12)	N(6)–C(45)	1.385(11)
g	C(16)–C(17)	1.453(13)	C(26)–C(27)	1.420(10)	C(38)–C(39)	1.420(27)

g_1	C(14)–C(15)	1.408(10)	C(28)–C(29)	1.436(15)	C(40)–C(41)	1.453(19)
h	C(15)–C(16)	1.334(9)	C(27)–C(28)	1.331(14)	C(39)–C(40)	1.276(23)
i	C(21)–C(22)	1.425(7)	C(33)–C(34)	1.423(11)	C(45)–C(46)	1.389(12)

(b) Angles

a b	N(2)–C(20)–C(19)	124.1(8)	N(3)–C(23)–C(24)	124.3(6)	N(5)–C(35)–C(36)	123(1)
$a_1 b_1$	N(1)–C(11)–C(12)	124.9(7)	N(4)–C(32)–C(31)	125(1)	N(6)–C(44)–C(43)	122.3(9)
b c	C(20)–C(19)–C(18)	118.8(6)	C(23)–C(24)–C(25)	117.5(8)	C(35)–C(36)–C(37)	119(1)
$b_1 c_1$	C(11)–C(12)–C(13)	118.1(6)	C(32)–C(31)–C(30)	118.3(9)	C(44)–C(43)–C(42)	119(1)
c d	C(19)–C(18)–C(17)	119.4(7)	C(24)–C(25)–C(26)	121(1)	C(36)–C(37)–C(38)	120(1)
$c_1 d_1$	C(12)–C(13)–C(14)	120.1(8)	C(31)–C(30)–C(29)	119.7(6)	C(43)–C(42)–C(41)	122(1)
d e	C(18)–C(17)–C(21)	119.0(8)	C(25)–C(26)–C(34)	117.5(7)	C(37)–C(38)–C(46)	119(1)
$d_1 e_1$	C(13)–C(14)–C(22)	118.4(6)	C(30)–C(29)–C(33)	118.5(8)	C(42)–C(41)–C(45)	118(1)
e f	C(17)–C(21)–N(2)	122.0(5)	C(26)–C(34)–N(3)	122.2(7)	C(38)–C(46)–N(5)	121.8(9)
$e_1 f_1$	C(14)–C(22)–N(1)	120.6(5)	C(29)–C(33)–N(4)	121.5(7)	C(41)–C(45)–N(6)	119.2(8)
f a	C(21)–N92)–C(20)	116.6(6)	C(34)–N(3)–C(23)	117.2(8)	C(46)–N(5)–C(35)	117.0(7)
$f_1 a_1$	C(22)8b1N(1)–C(11)	117.9(7)	C(33)–N(4)–C(32)	116.9(6)	C(45)–N(6)–C(44)	119.9(9)
e g	C(21)–C(17)–C(16)	119.1(5)	C(34)–C(26)–C(27)	119.6(8)	C(46)–N(5)–C(39)	119(1)
$e_1 g_1$	C(22)–C(14)–C(15)	117.8(5)	C(33)–C(29)–C(28)	119.8(7)	C(45)–C(41)–C(40)	118(1)
g h	C(17)–C(16)–C(15)	120.5(7)	C(–C927)–C(28)	122(1)	C(38)–C(39)–C(40)	124(1)
$g_1 h$	C(14)–C(15)–C(16)	122.7(9)	C(29)–C(28)–C(27)	120.4(7)	C(41)–C(40)–C(39)	119(1)
e i	C(17)–C(21)–C(22)	119.3(7)	C(26)–C(34)–C(33)	119.4(6)	C(38)–C(46)–C(45)	119(1)
$e_1 i$	C(14)–C(22)–C(21)	120.5(6)	C(29)–C(33)–C(34)	119.2(8)	C(41)–C(45)–C(46)	119.9(8)
d g	C(18)–C(17)–C(16)	121.9(7)	C(25)–C(26)–C(27)	123(1)	C(37)–C(38)–C(39)	122(1)
$d_1 g_1$	C(13)–C(14)–C(15)	123.8(8)	C(30)–C(29)–C(28)	121.7(6)	C(42)–C(41)–C(40)	124(1)
f i	N(1)–C(21)–C(22)	118.6(6)	N(3)–C(34)–C(33)	118.4(8)	N(5)–C(46)–C(45)	118.9(7)
$f_1 i$	N(1)–C(22)–C(21)	118.8(7)	N(4)–C(33)–C(34)	119.2(6)	N(6)–C(45)–C(46)	121(1)

separation 4.15 Å. Two phen molecules for each K atom complete the coordination sphere of this atom, which thereby has eight coordinated N atoms around it. The resulting coordination polyhedron forms a cube, as can be seen from Fig. 2. Such a cubic geometry has not been found before for the potassium ion.

Examination of the crystal packing (Fig. 3) shows a tendency of the phen molecules to lie parallel to one another within groups involving three of them. These are all planar within the error limits, with angles between planes as follows phen(1) phen(2) 4.4(1)°, phen(2) phen(3) 11.6(1)°, phen(1) phen(3) 7.5(1)°.
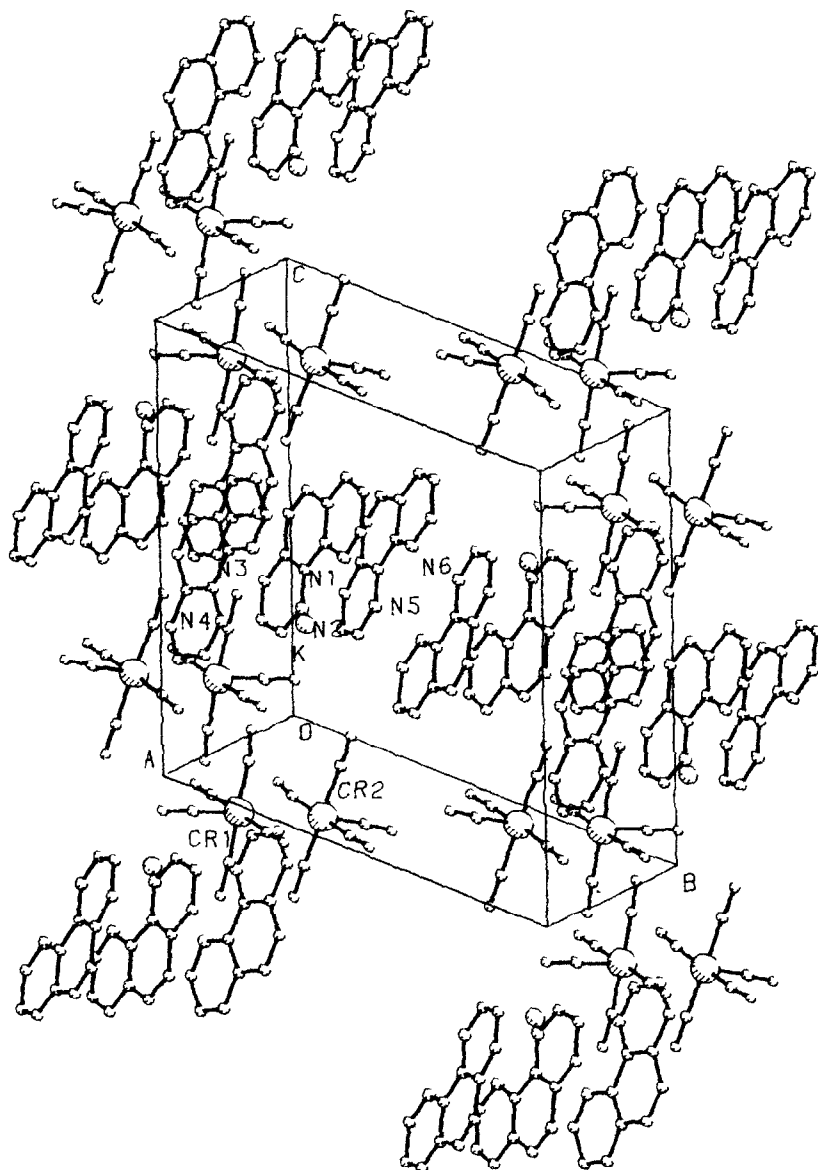
Fig. 2. Perspective view of the potassium coordination spheres in the dimeric centrosymmetric unit.

TABLE 5

INTERMOLECULAR CONTACTS BETWEEN phen MOLECULES OF LESS THAN 3.65 Å

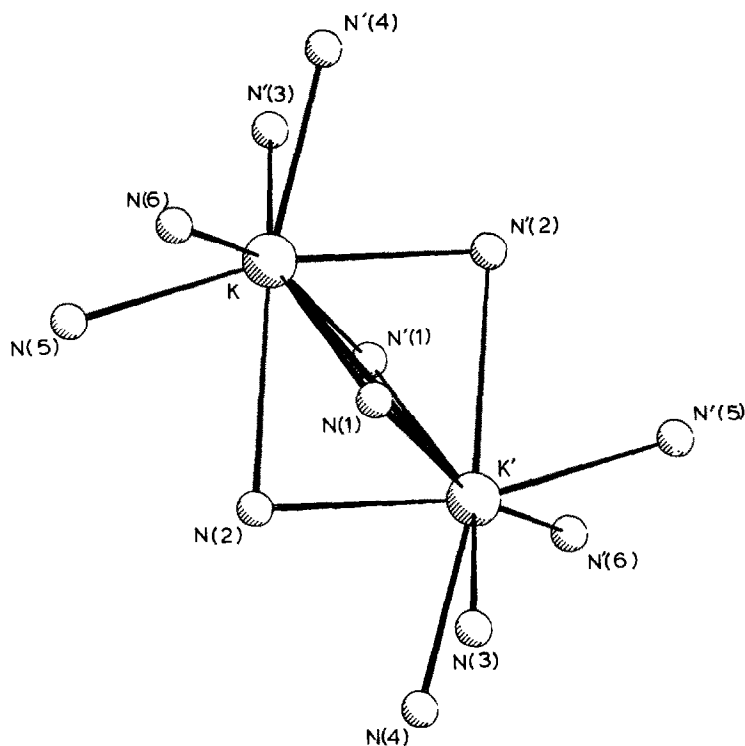| phen(1)–phen(2)		phen(1)–phen(3)	
C(11)–C(23)	3.38(1)	C(35)–C(19)	3.51(2)
C(12)–C(23)	3.54(1)	C(35)–C(20)	3.52(2)
C(13)–C(24)	3.39(1)	C(41)–C(15)	3.62(2)
C(14)–C(24)	3.48(1)	C(43)–C(13)	3.57(2)
C(14)–C(25)	3.51(1)	C(44)–C(12)	3.54(2)
C(15)–C(25)	3.56(1)	C(44)–C(13)	3.48(2)
C(16)–C(27)	3.65(1)	C(44)–C(14)	3.58(1)
C(17)–C(27)	3.63(1)	C(45)–C(14)	3.62(1)
C(18)–C(28)	3.67(1)	C(45)–C(22)	3.65(1)
C(19)–C(29)	3.50(1)	C(46)–C(17)	3.46(1)
C(19)–C(30)	3.60(1)	C(46)–C(21)	3.61(1)
C(20)–C(29)	3.62(1)		
C(20)–C(33)	3.51(1)		
C(21)–C(33)	3.60(1)		
C(21)–C(34)	3.38(1)		
C(22)–C(23)	3.56(1)		
C(22)–C(34)	3.52(1)		

Fig. 3. Perspective view of the unit cell content.

TABLE 6

STRUCTURAL PARAMETERS FOR THE CROMIUM PENTACARBONYL DERIVATIVES

Compound	Cr...Cr (Å)	Cr–H (Å)	Cr–A–Cr (°)	Carbonyl conformations	Cr–C$_{eq}$	Cr–C$_{ax}$
[(PPh$_3$)$_2$N][Cr$_2$(CO)$_{10}$]CH$_2$Cl$_2$ [13]	2.97(1)(X-ray)			"staggered"	1.87av.	1.84
[Et$_4$N][Cr$_2$(CO)$_{10}$(μ-H)] [13]	3.406(9)(X-ray)			"eclipsed"	1.88av.	1.82(2)
[Et$_4$N][Cr$_2$(CO)$_{10}$(μ-H)] [19]	3.386(6)(neutron)	1.707(21) 1.737(19)	158.9(6)(bent)	"eclipsed"	1.898(3) av.	1.827(3)
[(PPh$_3$)$_2$N][Cr$_2$(CO)$_{10}$(μ-H)] [10]	3.349(13)(neutron) 3.359(2)(X-ray)	1.675 1.679	180^a	"eclipsed"	1.896(3) 1.881(4)	1.862(8) 1 817(8)
[(PPh$_3$)$_2$N][Cr$_2$(CO)$_{10}$(μ-H)] [14]	3.390(3)(neutron 17 K)	1.737(9) 1.750(8) 1.718(9) 1.729(11)	157.6(7) 153.9(10)	"eclipsed"	1.901(3)	1.841(2)
[K(crypt 222)][Cr$_2$(CO)$_{10}$(μ-H)] [11]	3.300(4)(neutron 20 K)	1.735(5) 1.723(5)	145.2(3)	"staggered" 19°	1.900(3)	1.846(3)
K[Cr$_2$(CO)$_{10}$(μ-H)] [12]	3.350(linear av. (X-ray) 3.260(bent)	1.65(7) 1.90(7)	linear 132(3)	"eclipsed" "staggered" 36°	1.88(2)	1 88(1)

^{a} The high values of the hydrogen thermal parameters perpendicular to the Cr–Cr axis suggest a bent structure.

The values of the intermolecular contacts (Table 6) indicate that there are several contacts shorter than 3.6 Å (minimum value, 3.38 Å) between the bridging phen(1) molecule and the two adjacent phen(2) and phen(3) molecules facing it. Such an arrangement is similar to that found in the structure of the free phen [8]; in the latter there are short intermolecular contacts (minimum value, 3.31 Å) among the phen molecules which, since they are characteristic of graphitic type interactions have been taken to be an indication of the presence in the phen crystals of dipole–dipole interactions. Such interactions might be present also in $[K(phen)_3][Cr_2H(CO)_{10}]$. The coordination geometry of the potassium ion would then be constrained by such a phen packing effect, stabilizing a cubic geometry which is otherwise disfavoured.

The bulky $[K(phen)_3]^+$ cation appears to have an influence on the anion's solid-state configuration in a direction not favouring crystallographically imposed symmetries, unlike the Et_4N^+ [9] and PPN^+ [10] (bis(triphenylphosphine)im-minium) derivatives in which the presence of a crystallographic centre of inversion between the two Cr atoms leads to a statistical disposition of the μ-H atom around this center.

No direct interaction between the K^+ and the carbonyl oxygen atoms of the anion is observed. Under these circumstances, and in the absence of crystallographic site symmetry, the monoanion has adopted a bent Cr–H–Cr configuration with the equatorial carbonyls of the two independent $Cr(CO)_5$ groups, eclipsed and facing each other. The Cr...Cr distance of 3.394(3) Å as well as the Cr–H separations of 1.74(7) and 1.71(7) Å are comparable to the corresponding distances (3.390(3), 1.739(9) and 1.718(9) Å, respectively) found by neutron diffraction studies at 17 K for $[Cr_2(CO)_{10}(\mu-D)]^-$ as PPN^+ salt [10]. Also the Cr–H–Cr bond angle of 159(3)° is comparable in magnitude to those found for the deuterated species (157.6(7) and 153.9(10)°), as well as the average $Cr-CO_{eq}$ distance of 1.88(1) Å and the $Cr-CO_{ax}$ distance of 1.82(1) Å (1.901(3) and 1.841(2) Å, respectively).

A comparison of the structural data found for $[Cr_2(CO)_{10}(\mu-H)]^-$ (Table 6) in its Et_4N^+ [9], PPN^+ [10], K(crypt222) [11], and K^+ [12] salts reveals further features of the geometry of the monoanion. The Cr...Cr separation of 3.39 Å appears to be remarkably consistent with a bent-eclipsed metal carbonyl configuration. A shorter Cr...Cr separation, and so a decreased Cr–H–Cr bond angle, is consistent with a bent-staggered configuration, like that observed for the $[Cr_2(CO)_{10}(\mu-H)]^-$ anion in the $[K(crypt222)]^+$ salt [11]. Further, the extent of rotation of the equatorial carbonyls in each $Cr(CO)_5$ moiety depends on the Cr...Cr separation; a reduction in this separation implies a corresponding increase in the rotation of the two independent $Cr(CO)_5$ groups. In fact, the Cr...Cr separation of 3.300(4) Å in $[K(crypt222)][Cr_2H(CO)_{10}]$ [11] is accompained by a Cr–H–Cr bond angle of 145.2(3)° and a rotation of ca. 19° of the two independent $Cr(CO)_5$ groups, whereas the Cr...Cr separation of 3.260 Å in $K[Cr_2H(CO)_{10}]$ [12] is accompained by a Cr–H–Cr bond angle of 132(3)° with $Cr(CO)_5$ groups rotated by ca. 36°. From the results of our structural study it can thus be concluded that, in the absence of cation–anion interactions and of crystallographically imposed symmetries, the geometry of monoanion in $[K(phen)_3][Cr_2H(CO)_{10}]$ is of the bent-eclipsed type with a corresponding Cr...Cr separation of 3.39 Å; this value is confirmed by neutron diffraction data at low temperature.

Our results in addition to confirming the presence of the $[K(phen)_3]^+$ cation dimer in the compound, also provide evidence for a cubic arrangement around the K

atoms of the dimeric unit, $[K(phen)_3]_2^{2+}$. This is the first example of compound in which its potassium complex ion exhibits a cubic geometry, energetically less favoured than the square-antiprismatic one. As for the complex anion, $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$, evidence has been obtained for a previously unobserved geometry of the bent-eclipsed type.

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