

Fig. 1. Perspective view of the Ni complex with atom numbering. The solvate molecules have been omitted.

with atomic numbering is shown in Fig. 1. As Ni lies on an inversion centre, the coordinating isocyanide C atoms are coplanar with Ni, and the arrangement is approximately square-planar as follows from the C—Ni—C angle of 92.2 (3)°. The isocyanide ligands deviate from the C—Ni—C plane, the distances of N(1) and N(2) to this plane are 0.03 (1) and 0.10 (1) Å respectively and the Ni—C—N angles are 176.0 (5) and 174.0 (6)° respectively. The Ni—C distances [1.831 (8) and 1.839 (6) Å], the terminal N—C distances [1.152 (10) and 1.157 (9) Å] and the C—N—C angles [174.0 (7) and 174.3 (7)°] of the isocyanide ligands are similar to those observed in Ni⁰ isocyanide complexes. In bis(*tert*-butylisocyanide)(azobenzene)nickel(0) (Dickson & Ibers, 1972) the corresponding values are

1.842 (5), 1.839 (5); 1.155 (6), 1.156 (6) Å and 175.3 (5), 177.5 (6)°, and in bis(*tert*-butylisocyanide)-(N-*tert*-butyldicyanoketenimine)nickel(0) (Yarrow, Ibers, Tatsuno & Otsuka, 1973) the values are 1.819 (5), 1.876 (4); 1.149 (5), 1.147 (5) Å and 176.5 (4), 174.8 (4)°. The observed terminal C—N bond lengths lie in the range expected for C—N triple bonds. The N(1)—C(11) and N(2)—C(21) distances are 1.411 (9) and 1.396 (10) Å respectively and these are shorter than the corresponding distances in the Ni⁰ complexes, where these distances involve C(sp³) atoms. The angles between the phenyl rings and the C(1)—Ni—C(2) plane are 57.0 (4) (C₁₁→C₁₆) and 71.9 (4)° (C₂₁→C₂₆) respectively. The angle between the phenyl rings is 67.3 (4)°.

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A Tetracarbonyl(η^4 -dienone)chromium Complex

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Abstract. Tetracarbonyl[1-3,9a- η -(2,3-diethyl-4a,9a-dihydro-1-methoxy-4a,9-dimethyl-4H-carbazol-4-one)]-chromium(0), [Cr(CO)₄(C₁₉H₂₃NO₂)], *M_r* = 461.4, monoclinic, *P*2₁/*c*, *a* = 15.2045 (7), *b* = 8.4622 (3), *c* = 17.3682 (8) Å, β = 92.28 (1)°, *V* = 2232.9 (2) Å³, *Z* = 4, *D_x* = 1.37 g cm⁻³, Ni-filtered Cu *K* α radiation, λ = 1.5418 Å, μ = 45.5 cm⁻¹, *F*(000) = 960, *T* =

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295 K. Refinement of 284 parameters based on 2472 observed intensities gave a final *R* = 0.055. The diene is π -bonded to Cr in this [Cr(dienone)(CO)₄] complex, and angles and average bond lengths from Cr to carbonyl C atoms *trans* to the diene are 100.9 (2)° and 1.842 (6) Å, and to the *cis*-carbonyl C atoms are 155.4 (2)° and 1.886 (7) Å. This is the first structure

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reported for a metal complex isolated from annulation reactions of Cr indolyl carbene complexes with acetylenes.

Introduction. The *Aspidosperma* alkaloids are the largest group of indole alkaloids and they have been the target of numerous synthetic efforts (Wulff, 1988; Saxton, 1986). Both the *Aspidosperma* and *Strychnos* families display the common structural feature of a six-membered carbocyclic ring fused at the 2,3-positions of the indole nucleus. A new synthesis of an indole-fused six-membered ring has resulted from reaction of a chromium carbene complex with diethylacetylene (Bauta, Wulff, Pavkovic & Zaluzec, 1988). The reaction also produced the chromium complex whose structure is reported here. This compound showed some evidence of being a vinyl ketene intermediate. The ^{13}C NMR solution spectrum was inconclusive in this regard, but did reveal equivalent carbonyl groups. The structure determination was undertaken to establish the identity of the solid and to use that information to gain a better understanding of the reaction.

Experimental. A $0.35 \times 0.40 \times 0.35$ mm specimen was selected from good quality orange prismatic crystals (from ether) provided by Professor W. D. Wulff and W. E. Bauta (University of Chicago); general solubility precluded density measurements. A modified four-circle Picker diffractometer was used. Lattice parameters were determined from scans of $\pm 2\theta = |60-70^\circ|$ for 24 reflections, and relative absorption corrections varying from 1.0 to 0.70 were derived from φ scans at $\chi = 90^\circ$. Intensity data were collected by the $\theta-2\theta$ method to $[(\sin\theta)/\lambda]_{\max} = 0.56 \text{ \AA}^{-1}$ for $h -17 \rightarrow 17$, $k 0 \rightarrow 9$, $l 0 \rightarrow 19$ on 4473 reflections ($R_{\text{int}} = 0.024$) which contained 3322 unique and 2472 observed intensities [$F > 3\sigma(F)$]; four standard reflections showed 1% intensity variation over the data-collection period. The structure solution

Table 1. *Final atomic coordinates* ($\times 10^4$, $\times 10^5$ for Cr) and *equivalent isotropic thermal parameters* ($\text{\AA}^2 \times 10^3$, $\times 10^4$ for Cr)

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr	18812 (4)	17447 (8)	12164 (3)	429 (7)
O(1)	35 (2)	1375 (4)	532 (2)	80 (4)
O(2)	2212 (2)	-754 (4)	36 (2)	83 (4)
O(3)	1109 (3)	-140 (4)	2477 (2)	96 (4)
O(4)	3561 (3)	287 (5)	1883 (3)	118 (7)
O(5)	1619 (2)	4057 (3)	-172 (1)	48 (3)
O(6)	3287 (2)	3911 (4)	2710 (2)	60 (4)
N	3545 (2)	3263 (4)	147 (2)	43 (4)
C(1)	729 (3)	1590 (4)	781 (2)	51 (4)
C(2)	2080 (3)	205 (6)	490 (3)	55 (5)
C(3)	1404 (3)	559 (5)	1981 (2)	61 (5)
C(4)	2961 (4)	958 (6)	1630 (3)	64 (6)
C(5)	2917 (3)	4012 (5)	2080 (2)	46 (5)
C(6)	1945 (3)	3921 (5)	1964 (2)	43 (4)
C(7)	1543 (2)	4245 (4)	1233 (2)	38 (3)
C(8)	2035 (2)	3984 (5)	551 (2)	40 (4)
C(9)	2934 (3)	3748 (5)	649 (2)	38 (4)
C(10)	3420 (3)	4402 (5)	1362 (2)	37 (4)
C(11)	4312 (3)	3691 (6)	1288 (3)	44 (5)
C(12)	5042 (3)	3635 (7)	1786 (3)	66 (7)
C(13)	5797 (3)	2923 (8)	1531 (4)	84 (9)
C(14)	5836 (4)	2312 (8)	819 (4)	78 (8)
C(15)	5118 (3)	2368 (7)	295 (3)	68 (7)
C(16)	4363 (3)	3074 (6)	552 (3)	48 (5)
C(17)	1459 (3)	4018 (5)	2707 (2)	58 (5)
C(18)	1529 (4)	5594 (7)	3120 (3)	96 (8)
C(19)	612 (2)	4933 (4)	1130 (2)	51 (4)
C(20)	608 (3)	6710 (5)	1179 (3)	78 (6)
C(21)	1815 (3)	5469 (5)	-576 (2)	63 (5)
C(22)	3472 (3)	6202 (6)	1311 (3)	56 (5)
C(23)	3373 (3)	2572 (6)	-611 (2)	63 (6)

utilized the *SHELX76* computer program (Sheldrick, 1976), Patterson and Fourier synthesis methods, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), refinement on $|F|$ with $w = 0.87/[\sigma^2(F) + 0.0029F^2]$, calculated H-atom positions with group isotropic temperature factors refined for aryl and methylene H, and refinement of 284 parameters. The final results were $R = 0.055$, $wR = 0.061$, $S = 0.92$, $(\Delta/\sigma)_{\max} < 0.10$ and $\Delta\rho$ max./min. of $0.38/0.27 \text{ e \AA}^{-3}$.

Discussion. The structure of this $[\text{Cr}(\text{dienone})(\text{CO})_4]$ complex, compound (I), is shown in Fig. 1. Atomic coordinates and geometrical parameters are listed in Tables 1 and 2.* The C(6)···C(9) atoms from the diene portion of the ligand are π -bonded to Cr at two adjacent coordination sites *trans* to carbonyls C(2) and C(3). In turn these carbonyl C atoms have shorter bond lengths to Cr than do the mutually *cis* carbonyls C(1) and C(4). Such differences in bond lengths from Cr to *cis*- and *trans*-carbonyl C are common features in $[\text{Cr}(\text{bidentate ligand})(\text{CO})_4]$ complexes (Brown, 1978). Clearly the molecule shows fluxional behavior in solution (see above).

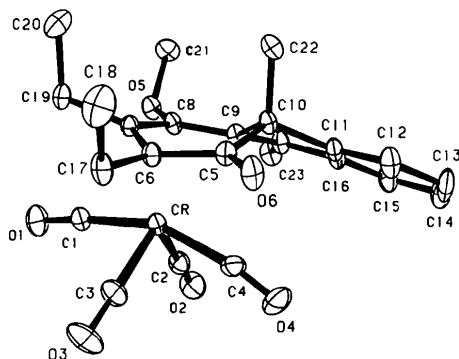


Fig. 1. ORTEP (Johnson, 1976) diagram of the compound. For sake of clearness the H atoms have been omitted from the diagram, and atoms C(7) and N [between C(10) and C(23)] are unlabeled. Thermal ellipsoids are scaled to enclose 30% probability.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51335 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å), angles (°) and selected torsion angles (°)

Cr—C(1)	1.884 (4)	N—C(23)	1.456 (5)
Cr—C(2)	1.847 (5)	C(5)—C(6)	1.486 (5)
Cr—C(3)	1.837 (4)	C(5)—C(10)	1.523 (5)
Cr—C(4)	1.887 (6)	C(6)—C(7)	1.414 (5)
Cr—C(5)	2.870 (7)	C(6)—C(17)	1.513 (5)
Cr—C(6)	2.261 (6)	C(7)—C(8)	1.443 (5)
Cr—C(7)	2.183 (6)	C(7)—C(19)	1.535 (5)
Cr—C(8)	2.237 (6)	C(8)—C(9)	1.385 (5)
Cr—C(9)	2.557 (7)	C(9)—C(10)	1.522 (5)
Cr—C(10)	3.151 (8)	C(10)—C(11)	1.493 (6)
O(1)—C(1)	1.140 (5)	C(10)—C(22)	1.528 (6)
O(2)—C(2)	1.154 (5)	C(11)—C(12)	1.382 (6)
O(3)—C(3)	1.151 (5)	C(11)—C(16)	1.385 (6)
O(4)—C(4)	1.147 (6)	C(12)—C(13)	1.385 (7)
O(5)—C(8)	1.386 (4)	C(13)—C(14)	1.344 (7)
O(5)—C(21)	1.423 (4)	C(14)—C(15)	1.394 (7)
O(6)—C(5)	1.213 (4)	C(15)—C(16)	1.384 (6)
N—C(9)	1.362 (5)	C(17)—C(18)	1.516 (6)
N—C(16)	1.414 (5)	C(19)—C(20)	1.506 (5)
C(1)—Cr—C(2)	81.4 (2)	O(5)—C(8)—C(7)	120.4 (3)
C(1)—Cr—C(3)	82.3 (2)	O(5)—C(8)—C(9)	122.0 (3)
C(2)—Cr—C(3)	100.9 (2)	C(7)—C(8)—C(9)	117.5 (3)
C(1)—Cr—C(4)	155.4 (2)	N—C(9)—C(8)	131.3 (4)
C(2)—Cr—C(4)	81.3 (2)	N—C(9)—C(10)	108.0 (3)
C(3)—Cr—C(4)	83.9 (2)	C(8)—C(9)—C(10)	119.5 (3)
C(8)—O(5)—C(21)	112.8 (3)	C(5)—C(10)—C(9)	110.1 (3)
C(9)—N—C(16)	108.9 (3)	C(5)—C(10)—C(11)	118.1 (4)
C(9)—N—C(23)	126.7 (3)	C(9)—C(10)—C(11)	101.3 (3)
C(16)—N—C(23)	121.8 (4)	C(5)—C(10)—C(22)	107.0 (3)
Cr—C(1)—O(1)	174.7 (4)	C(9)—C(10)—C(22)	109.8 (3)
Cr—C(2)—O(2)	179.4 (4)	C(11)—C(10)—C(22)	110.3 (4)
Cr—C(3)—O(3)	177.7 (4)	C(10)—C(11)—C(12)	132.0 (4)
Cr—C(4)—O(4)	170.8 (5)	C(10)—C(11)—C(16)	108.5 (4)
O(6)—C(5)—C(6)	122.7 (4)	C(12)—C(11)—C(16)	119.5 (4)
O(6)—C(5)—C(10)	121.6 (4)	C(11)—C(12)—C(13)	118.1 (5)
C(6)—C(5)—C(10)	115.5 (3)	C(12)—C(13)—C(14)	121.9 (5)
C(5)—C(6)—C(7)	120.2 (3)	C(13)—C(14)—C(15)	121.8 (5)
C(5)—C(6)—C(17)	113.6 (3)	C(14)—C(15)—C(16)	116.2 (5)
C(7)—C(6)—C(17)	123.1 (3)	N—C(16)—C(11)	109.6 (4)
C(6)—C(7)—C(8)	119.3 (3)	N—C(16)—C(15)	127.8 (4)
C(6)—C(7)—C(19)	122.8 (3)	C(11)—C(16)—C(15)	122.6 (4)
C(8)—C(7)—C(19)	117.9 (3)	C(6)—C(17)—C(18)	115.1 (4)
C(10)—C(5)—C(6)—C(7)	2.4 (7)	C(7)—C(8)—C(9)—C(10)	24.7 (7)
C(5)—C(6)—C(7)—C(8)	27.0 (7)	C(8)—C(9)—C(10)—C(5)	46.4 (7)
C(6)—C(7)—C(8)—C(9)	-13.2 (7)	C(9)—C(10)—C(5)—C(6)	-31.2 (7)

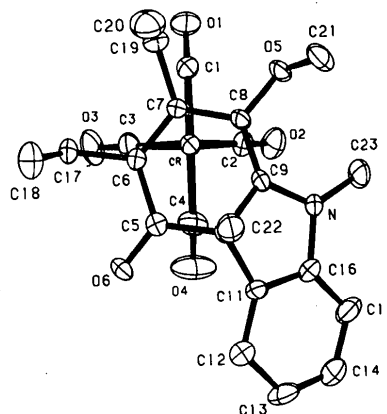


Fig. 2. ORTEP (Johnson, 1976) diagram viewed down the C(10)—C(22) bond, showing the rotated aspect of the ligand relative to the C(2)—Cr—C(3) plane of atoms. Thermal ellipsoids are scaled to enclose 30% probability.

There is good evidence for electron delocalization in the dienone region of the ligand. The three bonds linking C(6) through C(9) have an average bond length of 1.413 (9) Å and corresponding bond order of 1.52 (Pauling, 1960) symptomatic of aromatic character. Similar ring C—C distances of 1.417 (3) and 1.423 (1) Å are found in the arene complexes [Cr(benzene)₂], compound (II) (Keulen & Jellinek, 1966), and [Cr(benzene)(CO)₃], compound (III) (Rees & Coppens, 1973). In contrast, the olefinic complexes [Cr('Dewarbenzene')(CO)₄] (Huttner & Mills, 1971) and [Cr(7,7-dimethoxynorborn-2-ene)(CO)₄] (Brotherton, Wege, White & Maslen, 1974), have C—C distances of 1.36 (1) and 1.38 (1) Å. Aromatic character is also suggested for this region of (I) by its Cr— π -plane normal of 1.803 (1) Å which is to be compared with normals of 1.606 (1) and 1.73 Å reported for (II) and (III) (Muetterties, Bleeke, Wucherer & Albright, 1982). Delocalization in (I) may relax Cr—ligand alignment conditions and cause the slight turning of the ligand so that the central C(7)—C(8) bond of the π -bonded segment appears inclined 21° to the C(2)—Cr—C(3) plane. This is shown more clearly in Fig. 2.

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The C(6)···C(9) segment of the ligand π -bonded to Cr has several interesting features. This group of atoms is quite planar and the average deviation from the least-squares best-fit plane passing through them is only 0.04 (1) Å. Their plane is almost perpendicular [86.8 (1)°] to the C(2)—Cr—C(3) plane. This group of atoms is also part of a larger conjugated system which extends to C(5) and O(6). We believe this to be the first example reported for a [Cr(diene)(CO)₄] complex in which the π -bonded diene is a component of an extended conjugated chain, and where that extension does not participate in coordination to the metal.

The bond angles from Cr to *trans*- and *cis*-carbonyl C atoms of 100.9 (2) and 155.4 (2)° differ markedly from the 90 and 180° of a regular octahedron. In this regard compound (I) is the most distorted six-coordinate [Cr(diene)(CO)₄] reported to date. The previously noted largest deviation from 180° is the angle of 167° found in [Cr(N,N,N',N'-tetramethylethylenediamine)(CO)₄] (Kruger, Gafner, De Villiers, Raubenheimer & Swanepoel, 1980).

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Structure of Diaqua[*N*-(*o*-carboxyphenyl)iminodiacetato]chromium(III) Trihydrate

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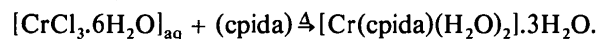
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Abstract. $[\text{Cr}(\text{C}_{11}\text{H}_8\text{NO}_6)(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, $M_r = 392.26$, orthorhombic, *Pbca*, $a = 14.2206$ (7), $b = 17.9251$ (7), $c = 12.3309$ (8) Å, $V = 3143.22$ Å³, $Z = 8$, $D_x = 1.657$, D_m (by flotation) = 1.655 g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5406$ Å, Ni filter, $\mu = 68.45$ cm⁻¹, $F(000) = 1600$, $T = 295$ K, $R = 0.0479$, $wR = 0.0513$ for 1409 observed reflections. The two water O atoms, the N atom and the three carboxyl O atoms of the quadridentate amino polycarboxylate ligand [*N*-(*o*-carboxyphenyl)iminodiacetic acid (cpida)] give distorted octahedral coordination around Cr. The Cr–O distances for the coordinated water molecules are nearly equal. The carboxyl O(2)–Cr distance is shorter than the other two glycinate O–Cr distances. The phenyl ring makes a dihedral angle of 109.5 (4)° with the equatorial coordination plane. The structure is stabilized by a network of hydrogen bonds involving the water molecules.

Introduction. Linear quadridentate amino polycarboxylic acids can wrap around metal ions in octahedral coordination in a variety of ways resulting in the formation of α -*cis*, β -*cis* and β - β *trans* configurations. In contrast to the extensive stereochemical studies involving linear amino polycarboxylic metal complexes, little study has been undertaken of complexes with tripod ligands. The amino polycarboxylate ligands have

donor groups similar to the more common amino acid residues and hence the studies of these complexes are of significance in comparison to amino acid complexes. The title complex can have two possible structures, Fig. 1. The structure determination was undertaken to establish the details of its coordination.

Experimental. The complex was synthesized by the literature method (Tomita, Kyuno & Tsuchia, 1969):



Recrystallization from water gave purple crystals. Intensity data (crystal dimensions 0.08 × 0.16 × 0.6 mm) were collected on an Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation, ω – 2θ scan.

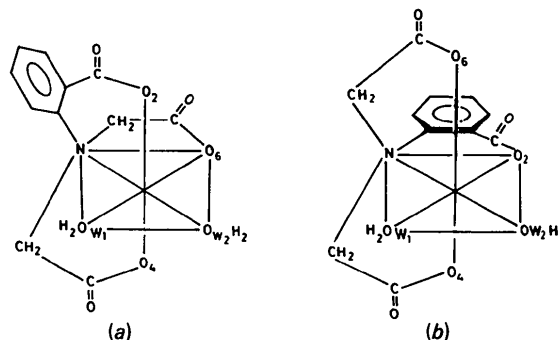


Fig. 1. Two possible structures.

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