0·002 (6) and 0·012 (5) Å out of the planes of the O atoms.

A similar structural arrangement to this has been observed in dinitratotris(pyridine)Cd^{II} (Cameron, Taylor & Nuttall, 1972) and also in aquadinitratobis(quinoline)Cd^{II} (Cameron, Taylor & Nuttall, 1973). The only structural results for 2,6-dimethyl-4-pyrone compounds are for the hydrobromide monohydrate (Hope, 1965) determined with limited X-ray data, dinitratobis(2,6-dimethyl-4-pyrone)zinc (Brown & Lewis, 1984*a*) and dinitratobis(2,6-dimethyl-4-pyrone)copper (Brown & Lewis, 1984*b*).

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Structures of *cis*-Dichloro(methanol)(salicylaldehyde benzoylhydrazonato)iron(III), $[FeCl_2(C_{14}H_{11}N_2O_2)(CH_4O)]$, and Chloro(salicylaldehyde benzoylhydrazonato)-copper(II) Monohydrate, $[CuCl(C_{14}H_{11}N_2O_2)].H_2O$

By A. A. Aruffo,* T. B. Murphy,† D. K. Johnson,‡ N. J. Rose and V. Schomaker

Departments of Chemistry and Medicinal Chemistry, University of Washington, Seattle WA 98195, *USA*

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Abstract. $[FeCl_2(Hsbh)(CH_3OH)]$ (*A*) (H_2sbh is *s*alicylaldehyde *b*enzoyl*h*ydrazone): $M_r = 398{\cdot}0$, triclinic, $P\bar{1}$, $a = 6{\cdot}665\,(2)$, $b = 13{\cdot}818\,(6)$, $c = 10{\cdot}122\,(4)$ Å, $\alpha = 108{\cdot}40\,(2)$, $\beta = 73{\cdot}23\,(2)$, $\gamma = 103{\cdot}32\,(2)^\circ$, $V = 837$ Å^3, $Z = 2$, $D_x = 1{\cdot}580$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12{\cdot}5$ cm^{-1}, $F(000) = 406$, room temperature. $[CuCl(Hsbh)].H_2O$ (*B*): $M_r = 356{\cdot}3$, monoclinic, $P2_1/a$, $a = 16{\cdot}201\,(21)$, $b = 7{\cdot}107\,(10)$, $c = 12{\cdot}540\,(18)$ Å, $\beta = 89{\cdot}87\,(9)^\circ$, $V = 1444$ Å^3, $Z = 4$, $D_x = 1{\cdot}64$ g cm^{-3}, $\mu = 17{\cdot}7$ cm^{-1}, $F(000) = 724$, room temperature. For (*A*), 3740 observations gave $R = 0{\cdot}043$ and $wR = 0{\cdot}036$. For (*B*), 1250 observations gave $R = 0{\cdot}091$ and $wR = 0{\cdot}065$. The Cu coordination in (*B*) is square-planar, with Cl^- and O(1), O(2), and N(2) of $Hsbh^-$; the Fe in (*A*) is octahedral, with axial Cl^- and CH_3OH in addition to Cl^-, O(1), O(2), and N(2) as in (*B*). The uncoordinated hydrazidic nitrogen, N(1), remains protonated in both.

Introduction. H_2sbh is a potentially tridentate chelating agent formed by the Schiff-base condensation of salicylaldehyde with benzoyl hydrazide. This agent produces a variety of biological responses, both in animals (Johnson, Pippard, Murphy & Rose, 1982), microorganisms (Dimmock, Baker & Taylor, 1972), and cultured cells (Ponka, Borova, Neuwirt, Fuchs & Necas, 1979; Johnson, Murphy, Rose, Goodwin & Pickart, 1982), which appear to be associated with its ability to chelate essential metal ions *in vivo*. Crystallographic studies of complexes (*A*) and (*B*), formed by H_2sbh with the common essential metals iron and copper, were therefore undertaken (preliminary communication: Aruffo, Murphy, Johnson, Rose & Schomaker, 1982) as part of our attempts to understand its biological properties. Although various transition-metal complexes of $Hsbh^-$ have been described, we know of no other $Hsbh^-$ crystal structures.§

Experimental. Crystals of (*A*) were obtained by mixing equimolar quantities of H_2sbh and $FeCl_3.6H_2O$ in methanol. The resulting solution was filtered; on

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* Present address: Department of Biochemistry, Harvard University, Cambridge, MA 02138, USA.

† Present address: Department of Chemistry, Ithaca College, Ithaca, NY 14850, USA.

‡ Department of Medicinal Chemistry. Present address: Abbott Laboratories, North Chicago, Illinois 60064, USA.

§ $Hsbh^-$: monoanion of H_2sbh (the H_2 here signifying the two acidic hydrogens).

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standing for 4 days at room temperature and then for 3 days at 278 K it yielded dark-green crystals of the product. A crystal of dimensions 0·52 (010) × 0·29 (011) × 0·29 (021) × 0·19 (101) mm was mounted on a glass fiber along **b**. Green-gray crystals of (*B*) were obtained as previously described (Iskander, El-Aggan, Refaat & El Sayed, 1975), by mixing and refluxing ethanolic solutions containing equimolar amounts of H_2sbh and $CuCl_2.2H_2O$ and allowing the resulting solution to stand overnight at room temperature. A crystal of dimensions 0·05 × 0·15 × 0·5 mm was selected and mounted along **b**. Precession and Weissenberg photographs were used for both compounds to obtain rough cell constants and to determine the space groups [absences for (*B*): $0k0$, $k = 2n + 1$, and $h0l$, $h = 2n + 1$]. Picker FACS-I diffractometer with Nb-filtered (0·007 cm) Mo $K\alpha$ radiation. Cell constants by least squares with high-2θ reflections at $\pm 2\theta$, 9 pairs for (*A*) and 15 for (*B*). Intensity data by θ–2θ scans at 2° $\min^{-1}$ in 2θ. For (*A*), 4327 inequivalent reflections in the range $2° < 2\theta < 57·5°$ ($\pm h$, $\pm k$, $+l$), with 10 s background counts fore and aft (scan width 1·4° plus α_1–α_2 dispersion) in the range $2° < 2\theta < 35°$ and 20 s background counts for the rest. Five standards monitored every 300 reflections gave $p = 0·5\%$, which was used in $\sigma_I^2 = s + t^2b + p^2I^2$, where σ_I is the standard deviation of the integrated intensity, s the scan count, t the scan/total–background time ratio, and b the total background count. For (*B*), 1996 inequivalent reflections in the range $3° < 2\theta < 45°$ ($\pm h$, $+k$, $+l$) with scan width 1·85° (plus α_1–α_2 dispersion), 20 s background counts, and four standards monitored every 300 reflections and giving $p = 0·5\%$. Programs of the *XRAY* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) were used for data reduction and all subsequent calculations (except placing the H atoms).

Table 1. *Atomic coordinates and* U_{eq} *values* (Å^2 ×10^2) *for* (*A*)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$†
Fe	0·15045 (7)	0·21569 (4)	0·09484 (5)	3·0
Cl(1)	0·06411 (12)	0·37712 (6)	0·12180 (9)	4·1
Cl(2)	−0·19182 (12)	0·13442 (6)	0·15789 (9)	3·9
O(1)	0·2008 (3)	0·2674 (2)	0·2997 (2)	3·6
O(2)	0·2111 (3)	0·1732 (2)	−0·1057 (2)	3·8
O(3)	0·2529 (3)	0·0746 (2)	0·0842 (2)	4·2
N(1)	0·5384 (4)	0·3154 (2)	0·1983 (3)	3·2
N(2)	0·4799 (4)	0·2704 (2)	0·0696 (3)	2·9
C(1)	0·4299 (5)	0·3537 (2)	0·4584 (3)	3·1
C(2)	0·6331 (5)	0·3835 (3)	0·4793 (4)	4·3
C(3)	0·6640 (6)	0·4243 (3)	0·6169 (4)	5·2
C(4)	0·4935 (7)	0·4339 (3)	0·7329 (4)	5·2
C(5)	0·2911 (6)	0·4044 (3)	0·7128 (4)	5·0
C(6)	0·2584 (5)	0·3647 (3)	0·5762 (3)	4·1
C(7)	0·3837 (5)	0·3100 (2)	0·3152 (3)	2·9
C(8)	0·6290 (5)	0·2581 (2)	−0·0463 (3)	3·4
C(9)	0·5890 (5)	0·2104 (2)	−0·1861 (3)	3·1
C(10)	0·7669 (5)	0·2036 (3)	−0·3038 (4)	4·3
C(11)	0·7427 (6)	0·1628 (3)	−0·4414 (4)	5·0
C(12)	0·5411 (6)	0·1285 (3)	−0·4650 (4)	4·8
C(13)	0·3661 (5)	0·1319 (3)	−0·3531 (3)	4·1
C(14)	0·3844 (5)	0·1719 (2)	−0·2110 (3)	3·2
C(15)	0·2184 (6)	0·0277 (3)	0·1985 (4)	5·8

† E.s.d.'s about 10%.

Table 2. *Atomic coordinates and* U_{eq} *values* (Å^2 ×10^2) *for* (*B*)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$†
Cu	0·0600 (1)	−0·1802 (2)	−0·3708 (1)	3·7
Cl	0·1833 (2)	−0·1111 (5)	−0·3066 (2)	4·8
O(1)	0·0001 (5)	−0·1073 (12)	−0·2410 (6)	4·4
O(2)	0·1045 (4)	−0·2731 (11)	−0·5000 (6)	4·0
O(3)	0·2522 (5)	0·0167 (13)	−0·5464 (6)	5·3
N(1)	−0·1094 (5)	−0·1292 (13)	−0·3512 (8)	3·3
N(2)	−0·0513 (5)	−0·1924 (15)	−0·4259 (8)	3·1
C(1)	−0·1314 (8)	−0·0290 (20)	−0·1679 (10)	4·2
C(2)	−0·2131 (7)	0·0170 (19)	−0·1809 (10)	4·6
C(3)	−0·2553 (8)	0·0866 (21)	−0·0948 (11)	5·8
C(4)	−0·2224 (8)	0·0909 (21)	0·0067 (11)	5·8
C(5)	−0·1438 (9)	0·0333 (24)	0·0195 (11)	7·2
C(6)	−0·0961 (7)	−0·0345 (20)	−0·0667 (10)	4·9
C(7)	−0·0768 (8)	−0·0959 (17)	−0·2557 (10)	3·6
C(8)	−0·0787 (6)	−0·2453 (17)	−0·5206 (10)	3·4
C(9)	−0·0212 (7)	−0·3102 (18)	−0·5999 (9)	3·1
C(10)	−0·0562 (7)	−0·3629 (21)	−0·6984 (10)	5·1
C(11)	−0·0105 (8)	−0·4236 (20)	−0·7819 (11)	5·6
C(12)	0·0743 (9)	−0·4299 (20)	−0·7715 (11)	5·6
C(13)	0·1098 (7)	−0·3795 (18)	−0·6761 (10)	4·1
C(14)	0·0657 (7)	−0·3138 (18)	−0·5894 (9)	2·8

† E.s.d.'s about 15%.

Analysis of the Patterson maps gave the sites of the metal atoms, which were then used to begin series of density maps from which the positions of all the other non-hydrogen atoms were obtained (Tables 1 and 2).* For (*A*), 10 of the 15 H atoms were placed with program *CALCAT* (Watenpaugh, 1972) at C—H = 0·95 Å, after which the remaining five (1, 151, 152, 153, 31) were found in a difference map and adjusted to a bond length of 0·95 Å (isotropic *U* values refined for all H atoms except 151, 152, 153, and 31, and all H positions held invariant except for 2, 8, 10, and 12). Full-matrix, least-squares refinement on *F* with $1/\sigma^2(F_o)$ weights, f', and f'', rejecting 587 reflections with F_o or $|F_c| < 3\sigma(F_o)$ led to $R = 0·043$, $wR = 0·036$, $S = 2·64$, last-cycle $(\Delta/\sigma)_{\rm ave} = 0·004$ and $(\Delta/\sigma)_{\rm max} = 0·05$, and subsequent difference map with no peak greater than 0·5 e Å^{-3} except in the vicinity of the Fe and Cl atoms, where the highest peaks were 1·7 and 0·7 e Å^{-3}, respectively. For (*B*), the H atoms (except for 1, 31, and 32, which were obtained from a difference map) were placed with *CALCAT* at 1·0 Å from their respective C atoms; all were assigned isotropic Gaussian amplitudes of $U = 0·10$ Å^2 and held invariant. The refinement, as described above, rejecting 746 reflections

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* Lists of F_o and F_c, H positions and *U* values, and anisotropic *U* values for the other atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39262 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with F_o or $|F_c| < 3\sigma(F)$ and 35 with *XRAY* 'WDF' > 12 – *i.e.* with $\Delta(F)/\sigma(F_o) > 12/2{\cdot}8 = 4{\cdot}3$, in view of FREL SC = 2·8 (this second set of rejected reflections were included in the *R* values and final difference map)* – led to $R = 0{\cdot}091$, $wR = 0{\cdot}065$, $S = 1{\cdot}45$, last-cycle $(\Delta/\sigma)_{\text{ave}} = 0{\cdot}025$ and $(\Delta/\sigma)_{\text{max}} = 0{\cdot}24$, and subsequent difference-map density everywhere less than 0·7 e Å^{-3}. The ellipsoid of C(14), Fig. 2, is thin (*U* went non-positive-definite and was automatically 'corrected' by *XRAY* program *CRYLSQ*). The trouble persisted when, with the idea that the refinement might have stalled on some wrong *F* signs, the model was arbitrarily distorted and re-refined. This not highly unusual difficulty may be a matter of routine random errors in the intensities, the total number of variables being 190 and the apparent error in the *U* eigenvalue being only 3σ or maybe less (some of the apparently normal $U_{ii}/\sigma_{U_{ii}}$ values are only a little more than 3). The probability of one of the variables being in error by 3σ is then about $190 \times 0{\cdot}0014 = 0{\cdot}27$, not extremely small.

No absorption correction was made in either case. Anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974); form factors for Cu and Fe from Doyle & Turner (1968), for Cl, O, N, and C from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965).

Discussion. In both (*A*) and (*B*), Hsbh$^-$ is bound to the metal ion by O(1), O(2), and N(2) in an approximately planar arrangement (Tables 3, 4 and 5). The uncoordinated hydrazidic nitrogen atom N(1) remains protonated, so that the organic ligand bears a formal electronic charge of –1. The remaining coordination site in the Hsbh$^-$ plane is occupied, in both structures, by a chloride ion (Figs. 1 and 2). In (*A*), the coordination polyhedron is completed by a second chloride ion Cl(1) and the O atom of a methanol molecule.

The octahedral structure of (*A*) is distorted tetragonally along the O(3)—Fe—Cl(1) axis, the Fe atom being displaced 0·134 Å from the least-squares equatorial plane defined by O(1), N(2), O(2), Cl(2), and Fe (Tables 3 and 5), as well as in the equatorial plane, angle O(1)—Fe—O(2) being only 159·3°, with O(2)—Fe—N(2) larger than O(1)—Fe—N(2), as would be expected from the different sizes of the two chelate rings.

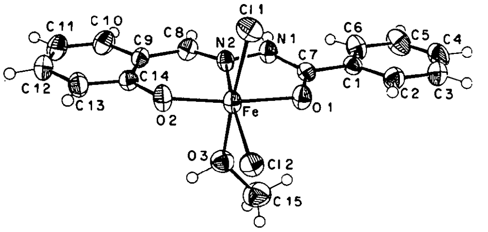

Fig. 1. *ORTEP* drawing (Johnson, 1965) of $[FeCl_2(Hsbh)(CH_3OH)]$ (*A*). Note that the numbering of the two chloride ions is the reverse of that used in the preliminary communication of this structure (Aruffo *et al.*, 1982).

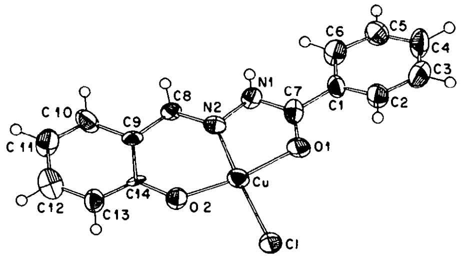

Fig. 2. *ORTEP* drawing of the [CuCl(Hsbh)] unit present in (*B*).

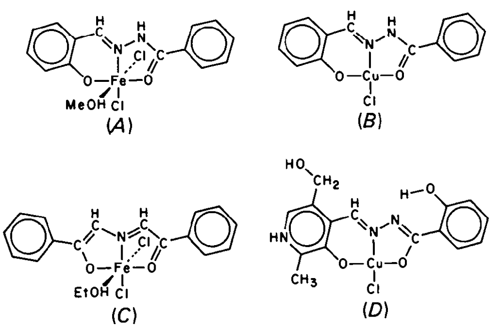

Fig. 3. Line drawings of the title compounds and their analogs.

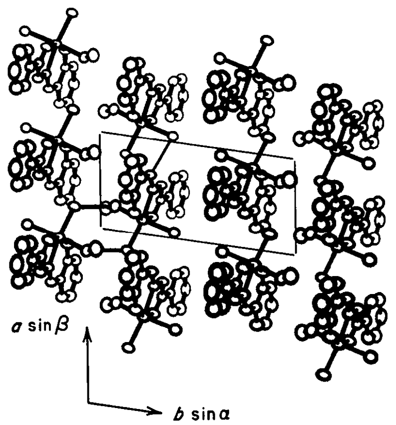

Fig. 4. Packing of (*A*), viewed along **c**. One of the N(1)—H···Cl(1) hydrogen bonds and two of the O(3)—H···Cl(2) are marked by solid lines.

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* The output F_o *vs* F_c listing from the *XRAY* least-squares program has a column headed 'WDF' and described in the *XRAY* manual as $(F_o - F_c)/\sigma(F_o)$ (in *XRAY* 'W' is the square root of the Gaussian weight), but which is actually this quantity multiplied by the relative scale factor $F/F_{\text{rel}} = F/\sqrt{(I/\text{Lp})}$ = 'FREL SC'. Whereas the manual says that a reflection will be rejected 'if its weighted delta-*F* is larger than' a quantity specified by the user (here 12), it is 'WDF' that is tested, and, contrary to reasonable expectation, reflections so rejected from the refinement are nonetheless included in the statistics of fit. Many users of *XRAY* are doubtless unaware of this.

In an analogous complex with two five-membered chelate rings, (*C*) (Fig. 3), the O(1)—Fe—O(2) angle is even smaller at 151° (Bertrand, Fujita, Eller & VanDerveer, 1978). Because O—Fe—O is less than 180°, contacts between the equatorial chloride ion and O(1) and O(2) are only slightly shorter than the sum of the van der Waals radii of oxygen and chlorine. In contrast, distances between the axial chloride ion and the equatorial ligating atoms are considerably less than the respective sums of van der Waals radii. This difference in ligand–ligand repulsions may account for the equatorial Fe—Cl bond being significantly shorter than the axial Fe—Cl bond in both (*A*) and (*C*). The intermolecular hydrogen bonding of (*A*) forms a ladder pattern (Fig. 4): each side piece, as deep as the length of

Table 3. *Bond distances* (Å) *and angles* (°) *for* (*A*)

Coordination polyhedron			
Fe—O(1)	2·068 (2)	Fe—N(2)	2·119 (2)
Fe—O(2)	1·874 (2)	Fe—Cl(1)	2·345 (1)
Fe—O(3)	2·171 (3)	Fe—Cl(2)	2·303 (1)
Ligand			
O(1)—C(7)	1·256 (4)	N(2)—C(8)	1·293 (3)
C(7)—C(1)	1·477 (4)	C(8)—C(9)	1·434 (4)
C(1)—C(2)	1·379 (5)	C(9)—C(10)	1·414 (4)
C(2)—C(3)	1·384 (5)	C(10)—C(11)	1·370 (5)
C(3)—C(4)	1·374 (5)	C(11)—C(12)	1·381 (6)
C(4)—C(5)	1·371 (6)	C(12)—C(13)	1·369 (4)
C(5)—C(6)	1·378 (5)	C(13)—C(14)	1·399 (5)
C(6)—C(1)	1·390 (4)	C(14)—C(9)	1·409 (5)
C(7)—N(1)	1·336 (4)	C(14)—O(2)	1·326 (3)
N(1)—N(2)	1·380 (4)	C(15)—O(3)	1·437 (6)
Coordination polyhedron			
O(1)—Fe—Cl(1)	89·43 (8)	Cl(2)—Fe—Cl(1)	96·73 (4)
O(1)—Fe—O(3)	85·54 (10)	Cl(2)—Fe—O(3)	86·95 (7)
N(2)—Fe—Cl(1)	93·97 (8)	O(1)—Fe—N(2)	74·40 (9)
N(2)—Fe—O(3)	81·64 (10)	O(2)—Fe—N(2)	85·51 (9)
O(2)—Fe—Cl(1)	96·97 (9)	O(2)—Fe—Cl(2)	102·76 (7)
O(2)—Fe—O(3)	86·73 (10)	O(1)—Fe—Cl(2)	95·95 (6)
O(2)—Fe—O(1)	159·31 (9)	O(3)—Fe—Cl(1)	174·06 (7)
N(2)—Fe—Cl(2)	165·53 (9)		
Chelate rings			
C(7)—O(1)—Fe	118·3 (2)	C(8)—N(2)—Fe	128·8 (2)
O(1)—C(7)—N(1)	118·5 (3)	N(2)—C(8)—C(9)	123·1 (3)
C(7)—N(1)—N(2)	115·4 (2)	C(8)—C(9)—C(14)	123·6 (2)
N(1)—N(2)—Fe	113·1 (2)	C(9)—C(14)—O(2)	122·6 (3)
N(1)—N(2)—C(8)	117·8 (2)	C(14)—O(2)—Fe	136·1 (2)
Ligand			
C(1)—C(2)—C(3)	119·8 (3)	C(8)—C(9)—C(10)	117·1 (3)
C(2)—C(3)—C(4)	120·4 (4)	C(9)—C(10)—C(11)	121·0 (3)
C(3)—C(4)—C(5)	120·1 (4)	C(10)—C(11)—C(12)	119·3 (3)
C(4)—C(5)—C(6)	120·0 (3)	C(11)—C(12)—C(13)	121·0 (3)
C(5)—C(6)—C(1)	120·3 (3)	C(12)—C(13)—C(14)	121·4 (3)
C(6)—C(1)—C(2)	119·4 (3)	C(13)—C(14)—C(9)	117·9 (3)
C(6)—C(1)—C(7)	117·5 (3)	C(14)—C(9)—C(10)	119·3 (3)
C(2)—C(1)—C(7)	123·1 (3)	C(13)—C(14)—O(2)	119·5 (3)
C(1)—C(7)—O(1)	121·6 (2)	C(15)—O(3)—Fe	127·7 (2)
C(1)—C(7)—N(1)	119·9 (3)		

Table 4. *Bond distances* (Å) *and angles* (°) *for* (*B*)

Coordination polyhedron			
Cu—O(1)	1·962 (8)	Cu—N(2)	1·933 (9)
Cu—O(2)	1·891 (8)	Cu—Cl	2·211 (4)
Ligand			
O(1)—C(7)	1·263 (5)	N(2)—C(8)	1·323 (15)
C(7)—C(1)	1·489 (18)	C(8)—C(9)	1·437 (16)
C(1)—C(2)	1·373 (17)	C(9)—C(10)	1·410 (17)
C(2)—C(3)	1·370 (19)	C(10)—C(11)	1·352 (19)
C(3)—C(4)	1·381 (20)	C(11)—C(12)	1·381 (20)
C(4)—C(5)	1·349 (21)	C(12)—C(13)	1·375 (19)
C(5)—C(6)	1·411 (19)	C(13)—C(14)	1·381 (17)
C(6)—C(1)	1·394 (18)	C(14)—C(9)	1·415 (15)
C(7)—N(1)	1·332 (16)	C(14)—O(2)	1·319 (14)
N(1)—N(2)	1·401 (13)		
Coordination polyhedron			
O(1)—Cu—O(2)	171·8 (3)	N(2)—Cu—O(1)	81·3 (4)
O(1)—Cu—Cl	94·9 (3)	N(2)—Cu—O(2)	91·9 (4)
O(2)—Cu—Cl	92·6 (3)	N(2)—Cu—Cl	169·7 (3)
Chelate rings			
Cu—O(1)—C(7)	112·5 (8)	Cu—N(2)—C(8)	130·4 (7)
O(1)—C(7)—N(1)	120·9 (11)	N(2)—C(8)—C(9)	119·6 (9)
C(7)—N(1)—N(2)	113·0 (9)	C(8)—C(9)—C(14)	125·8 (10)
N(1)—N(2)—Cu	111·9 (7)	C(9)—C(14)—O(2)	123·5 (10)
N(1)—N(2)—C(8)	117·7 (8)	C(14)—O(2)—Cu	128·5 (7)
Ligand			
C(1)—C(2)—C(3)	118·1 (12)	C(8)—C(9)—C(10)	115·5 (10)
C(2)—C(3)—C(4)	122·8 (12)	C(9)—C(10)—C(11)	122·9 (11)
C(3)—C(4)—C(5)	118·0 (13)	C(10)—C(11)—C(12)	118·7 (13)
C(4)—C(5)—C(6)	121·9 (13)	C(11)—C(12)—C(13)	119·5 (13)
C(5)—C(6)—C(1)	117·6 (12)	C(12)—C(13)—C(14)	123·8 (12)
C(6)—C(1)—C(2)	120·8 (12)	C(13)—C(14)—C(9)	116·5 (10)
C(6)—C(1)—C(7)	114·9 (11)	C(14)—C(9)—C(10)	118·6 (10)
C(2)—C(1)—C(7)	124·0 (12)	C(13)—C(14)—O(2)	119·8 (10)
C(1)—C(7)—O(1)	119·8 (11)	C(1)—C(7)—N(1)	119·1 (11)

Table 5. *Dihedral angles* (°) *and selected deviations* (Å) *from least-squares planes*

The planes are defined by the following sets of atoms: I C(1)—C(6); II C(7), N(1), N(2), *M*, O(1); III N(2), C(8), C(9), C(14), O(2), *M*; IV C(9)—C(14); V O(2), N(2), O(1), Cl_{eq}, *M*.

(*A*) (*B*)	I	II	III	IV	E.s.d.*	*M*	O(2)	N(2)	O(1)	Cl_{eq}	Cl_{ax}
I					0·005	−0·115	−0·069	0·187	−0·234	−0·900	2·16
					0·040	0·458	0·344	−0·080	0·359	1·416	—
II	10·9				0·042	0·027	−0·101	−0·035	−0·030	−0·351	2·37
	14·1				0·047	0·027	−0·092	−0·042	−0·016	0·471	—
III	6·0	6·8			0·043	−0·039	0·023	0·046	−0·250	−0·606	2·27
	16·4	3·6			0·023	0·004	−0·019	0·002	−0·130	0·364	—
IV	3·3	8·0	2·9		0·014	−0·065	−0·033	0·117	−0·211	−0·726	2·23
	17·1	3·8	0·8		0·014	−0·006	−0·041	0·018	−0·124	0·326	—
V	14·8	4·4	9·8	11·7	0·127	0·134	0·008	−0·089	0·022	−0·076	2·47
	21·7	7·7	5·6	4·8	0·170	−0·041	−0·104	0·143	−0·110	0·122	—

* Scatter e.s.d. of a defining atom: $\sqrt{[(\sum d_i^2)/(n-3)]}$, the d_i being the *deviations* of the n defining atoms from the plane. This quantity is given incorrectly as $\sqrt{[(\sum d_i^2)/(n-1)]}$ by program *XRAY LSQPL*.

the ligand and consisting of a string of molecules along **a** joined by N(1)—H···Cl(1) bonds, 3·328 Å, is related to its oppositely directed mate by centers of symmetry, the rungs being centrosymmetric pairs of O(3)—H··· Cl(2) bonds at 3·174 Å. Although the N(1)···Cl(2) distance, 3·264 Å, is a bit shorter than N(1)···Cl(1), listed above, the probable N(1)—H···Cl(2) angle, with H in the ligand plane, is less than 90°, and the contact can hardly be called a bifurcated hydrogen bond. The ladders stack roughly rail-to-rail along **b** and face-to-face along **c**.

In (*B*), copper is approximately square planar (Tables 4 and 5), but, as is usual (Aruffo, Anderson, Lingafelter & Schomaker, 1983; Robertson & Truter, 1967), there are also close contacts with copper perpendicular to the coordination plane, in this case with both C(8) (3·330 Å) on one side of the plane and C(10) (3·360 Å) on the other. The oxygen [O(3)] of the water molecule in (*B*) is 3·851 Å distant from the Cu atom, which is at variance with the formulation of Iskander *et al.* (1975), who first reported the preparation of (*B*) and concluded from its IR spectrum that the water molecule was bound to the Cu atom. The closest analog of (*B*) for which structural data are available (Domiano, Musatti, Nardelli, Pelizzi & Predieri, 1979) is the complex $[(H_2psh)CuCl].H_2O$, (*D*) (Fig. 3, H_3psh is *p*yridoxal *s*alicyloyl*h*ydrazone) which, like (*B*), has an uncoordinated water molecule and, in respect to the immediate chelate system, differs only in that the proton on N(1) has been transferred to the heterocyclic N atom of the pyridoxal ring (Fig. 3). This transfer has, however, only small effects on the bond lengths and angles within the two chelate rings, the strong hydrogen bonds in the two structures [N—H···O, N(1)—O(3) = 2·766 Å in (*B*) and intramolecular N···H—O, N(1)—O(3) = 2·601 Å in (*D*)] apparently moderating the nominal differences in the bond orders of N(1)—C(7) and C(7)—O(1). The uncoordinated water molecule in (*B*) appears to form altogether three hydrogen bonds: with O(3)—H(31)···Cl [O(3)—Cl = 3·332 Å] and N(1)—H(1)···O(3) (already mentioned) it links the tightly stacked alternating molecules into columns along **b** (Fig. 5), and with O(3)—H(32)···O(2) [O(3)—O(2) = 2·823 Å] it joins these stacks along **a**, forming a two-dimensional hydrogen-bond network. [It must be said that O(3) also has a noticeably short distance, 3·389 Å, to another Cl^-, but that in view of the difference-map location of H(31) and the unfavorable implied bond angles, it is unlikely that this represents hydrogen bonding by a relocated H(31).] Along **c**, there are only van der Waals interactions between the interdigitating aromatic rings.

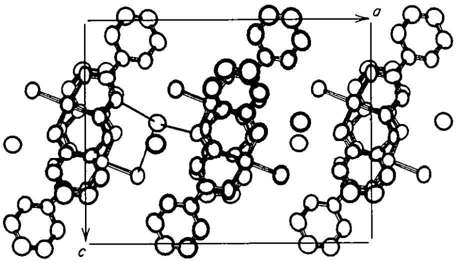

Fig. 5. Packing of (*B*), viewed antiparallel to **b**. The three hydrogen bonds to one of the O(3) atoms are marked by solid lines.

In (*A*), (*B*), and (*D*) the metal—O(2) bond is considerably shorter than the metal—O(1) bond, the difference being greater in (*A*) (0·19 Å) than in (*B*) (0·087 Å) and (*D*) (0·054 Å). This is consistent with more of the negative charge carried by the ligand being localized on O(2) than on O(1). Some degree of charge delocalization is, however, indicated by the C(14)—O(2) distances, which are shorter than expected for a single bond, and the C(7)—O(1) distances, which are longer than normal C=O double bonds. In (*C*), which intrinsically has end-for-end symmetry with a highly delocalized π system (Betrand *et al.*, 1978), the Fe—O(1) and Fe—O(2) distances are virtually identical, at 2·021 (4) and 2·037 (5) Å. The metal—nitrogen bond lengths in (*A*) and (*C*) average 2·128 Å, those in (*B*) and (*D*), 1·933 Å. Similarly, the mean metal—oxygen distances (for the equatorial donors) are longer in (*A*) and (*C*) (1·998 Å) than in (*B*) and (*D*) (1·924 Å). These shorter distances in the copper complexes probably reflect reduced ligand–ligand repulsion in four-coordinate complexes relative to six-coordinate compounds and the increased nuclear charge of the Cu atom, which makes it a better σ acceptor. The smaller difference between the metal—oxygen distances may arise because the high-spin Fe^{III} ion can have a net positive π interaction with the oxygen donors whereas the d^9 Cu^{II} ion cannot. Such favorable Fe—O π interactions may partially counteract the above-mentioned effects of coordination number and σ acceptor character and may account for the shortest metal—oxygen distance in the four complexes being found in (*A*) [Fe—O(2) = 1·874 Å].

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Structure of Tetrakis(2,6-dimethylphenyl isocyanide)rhodium(I) Tetraphenylborate Ethanol Solvate, $[Rh(C_9H_9N)_4][B(C_6H_5)_4].C_2H_6O$

BY TERENCE V. ASHWORTH, DAVID C. LILES, HESTER E. OOSTHUIZEN AND ERIC SINGLETON

National Chemical Research Laboratory, PO Box 395, Pretoria, Republic of South Africa

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Abstract. $M_r = 992{\cdot}92$, triclinic, $P\bar{1}$, $a = 11{\cdot}615\ (3)$, $b = 23{\cdot}582\ (5)$, $c = 10{\cdot}409\ (2)$ Å, $\alpha = 91{\cdot}20\ (2)$, $\beta = 104{\cdot}19\ (2)$, $\gamma = 102{\cdot}36\ (2)°$, $U = 2691{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}224$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}307$ mm^{-1}, $F(000) = 1040$, $T = 293$ K. Final $R = 0{\cdot}0554$ for 4321 observed reflections. The unit cell contains two independent monomeric square-planar cations lying across centres of inversion at 0,0,0 and $\frac{1}{2},\frac{1}{2}$,0 respectively. Because of steric crowding between *ortho* methyl groups on adjacent ligands, the phenyl rings of the ligands are not coplanar with the plane of coordination. The formation of Rh—Rh bonded oligomers is thus sterically inhibited.

Introduction. Tetraisocyaniderhodium(I) cations $[Rh(CNR)_4]^+$ tend to oligomerize in solution to form dimeric and trimeric species containing weak metal–metal bonds (Singleton & Oosthuizen, 1983). The extent of the oligomerization depends on the solvent, the concentration and the bulkiness of the substituent R, with the colour of the solutions ranging from yellow or orange (monomeric) to green, blue or purple (oligomeric). Crystal structures have been reported for the purple, blue and dark-green crystals of the dimers $[Rh(CNR)_4]_2^{2+}.2X^-$ with R = Ph, X = BPh_4 (II) (Mann, Lewis, Williams, Gray & Gordon, 1978), $R = p\text{-}FC_6H_4$, X = Cl (III) and $R = p\text{-}NO_2C_6H_4$, X = Cl (IV) (Endres, Gottstein, Keller, Martin, Rodemer & Steiger, 1979). However, our study represents the first crystal-structure determination of the monomeric form of $[Rh(CNR)_4]^+$.

Experimental. The reaction of [Rh(1,5-cyclooctadiene)Cl]$_2$ with excess C_8H_9NC in methanol yielded, on addition of $NaBPh_4$, the title complex (I). Yellow irregular-shaped crystals suitable for X-ray examination were grown from dichloromethane/ethanol solution. Crystal: fragment, 0·25 × 0·20 × 0·20 mm; Philips PW1100 four-circle diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation; lattice parameters: 25 reflections, least-squares refinement; ω–2θ scan mode, scan width 0·90° in ω, scan speed 0·03° s^{-1} in ω, 15s background at each end of the scan; 7347 reflections measured in the hemisphere $\pm h$, $\pm k$, $+l$ with $3 \le \theta \le 23°$, 7032 unique reflections, $R_{\text{int}} = 0{\cdot}019$; three standards measured every 60 min showed no significant deviations from mean intensities; no absorption correction applied; 4321 reflections $[F_o \ge 4\sigma(F_o)]$, index range $h \pm 12$, $k \pm 25$, l 0–11, used in analysis; structure solved by Patterson and Fourier methods and refined by least squares with *SHELX* (Sheldrick, 1978), two orientations observed for a disordered ethanol of solvation; site-occupation factors for the two orientations refined but constrained to sum to 1·0; all H-atom positions except for those in the disordered ethanol molecule located on a difference map and refined; anisotropic temperature factors used for all non-H atoms except in the disordered ethanol molecule where individual isotropic temperature factors were employed, separate common isotropic temperature factors used for the ring and methyl H atoms in each independent cation and for the H atoms in the BPh_4 anion; least-squares refinement, $\sum w(\Delta F)^2$

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