a common $U_{\rm iso}$ was refined for each molecule, and the water O atom. After initial room-temperature investigation of crystal quality, accurate low-temperature data collection was planned for a charge–density study. The crystal was cooled to 9 K using a Displex closed-cycle He cryostat mounted on a Huber diffractometer (Henriksen *et al.*, 1986). However, some effect causes reversible splitting of most intensity profiles below 200 K. A data set was therefore collected at 200 K. Disappointingly, the higher-order reflections were generally very weak and as further cooling was not considered helpful given the peak broadening effect, data were collected only to a 2θ limit of 43°. The structure was solved and a satisfactory refinement was obtained using these data. However, the 2θ limit was deemed to be unacceptably low and a further data set was therefore collected. The first attempt at collecting a new data set showed the original batch of crystals, which had been exposed to the atmosphere, to be polycrystalline despite retaining the appearance of single crystals, *i.e.* hard well formed with shiny faces. Data were therefore collected on a crystal from a second batch of crystals which had not been open to air. Data were collected at room temperature so as not to damage the crystal. Although there was obviously a similar problem with a rapid drop in intensity with increasing 2θ values, especially given the higher temperature, the use of an area detector allowed the collection of many more significant higher-order data in a reasonable length of time.

Data collection: *SMART* (Siemens, 1994); *MAD* (Allibon, 1995) for 200 K data. Cell refinement: *SMART*. Data reduction: *SORTAV* (Blessing, 1997) and *SAINT* (Siemens, 1994); *KRYSTAL* (Hazell, 1995) for 200 K data. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*.

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N—H···N, N—H···O and N—H···$\pi_{\rm CO}$ Hydrogen Bonding in [*N*,*N*-Bis(2-aminoethyl)-2-aminoethyl]ammonium Tetracarbonylcobaltate(1−)

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Abstract

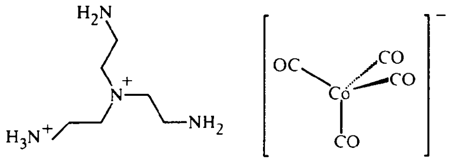
In the title compound, $(C_6H_{19}N_4)[Co(CO)_4]$, the cations are linked *via* N—H···N hydrogen bonds in a two-dimensional (2D) grid that takes the form of a buckled sheet. Channels between sheets are occupied by the $[Co(CO)_4]^-$ anions, which are linked to the cation network *via* N—H···O and N—H···$\pi_{\rm CO}$ hydrogen bonds. Both types of cation–anion hydrogen bond are uncommon. Indeed, this is the first report of a structurally characterized N—H···$\pi_{\rm CO}$ hydrogen bond.

Comment

Organometallic compounds are rich sources of hydrogen-bonding interactions. In some cases, hydrogen bonds between ligands can be similar to those found in the organic analogs (Braga *et al.*, 1994; Biradha *et al.*, 1996). However, in other cases, the metal can induce electronic changes in ligands such as halogens (Aullón *et al.*, 1998; Mareque Rivas & Brammer, 1998*c*), carbonyls (Braga *et al.*, 1995; Braga & Grepioni, 1997) and alkynyls (Müller *et al.*, 1994) *via* metal–ligand bonding interactions, which enhance interactions that are uncommon or weaker in organic compounds. Moreover, metals can participate directly as hydrogen-bond donors (Epstein *et al.*, 1993; Fairhurst *et al.*, 1995; Peris & Crabtree, 1995; Braga *et al.*, 1996) or acceptors (Calderazzo *et al.*, 1981; Brammer *et al.*, 1991, 1995; Wehman-Ooyevaar *et al.*, 1992; Kazarian *et al.*, 1993; Braga *et al.*, 1997).

Much of our recent work has been focused on investigating the types of hydrogen bonds in inorganic and organometallic compounds that exhibit features differing from hydrogen bonds in organic chemistry (Brammer *et al.*, 1991, 1992, 1995; Brammer & Zhao, 1994; Zhao *et al.*, 1996; Mareque Rivas & Brammer, 1998*b*,*c*; Aullón *et al.*, 1998).

In our earlier studies of ammonium salts of the $[Co(CO)_4]^-$ anion, we have focused primarily on the ability of the electron-rich d^{10} system Co^{-1} metal center to serve as a hydrogen-bond acceptor for the ammonium N—H group. We have also noted that the carbonyl O atoms are frequently involved in hydrogen bonding in these systems, particularly C—H···O hydrogen bonds. However, the anion possesses a third type of acceptor site, namely, the π electrons of the C≡O bonds. To our knowledge, hydrogen bonds involving this type of acceptor, analogous to known hydrogen bonds involving the π electrons of the acetylenic C≡C bonds, have not been discussed in the literature to date. In the present study, we report that $[(tren)H]^+[Co(CO)_4]^-$, (1), where tren is tris(2-aminoethyl)amine, exhibits N—H···O and N—H···π_{CO} hydrogen bonds linking the cations and anions (Fig. 1), as well as N—H···N hydrogen bonds connecting cation units to each other. A review of the supramolecular interactions of ammonium salts of the $[Co(CO)_4]^-$ anion can be found in Mareque Rivas & Brammer (1998*b*).


(1)

While the neutral tetraamine tren is a common chelating agent (for example, see Mareque Rivas & Brammer, 1998*a*), the crystal structure of (1) is, surprisingly, the first reported structure of a salt of $(tren)H^+$. The additional proton in (1) leads to a primary ammonium site on one of the three 'arms' of tren. This assignment is based upon H atoms located from the difference map and refined. The cations are linked to each other *via* two independent N^+—H···N hydrogen bonds, both originating from the ammonium center, N2, and linking to N3 and N4 of two neighboring cations. These hydrogen bonds give rise to a two-dimensional (2D) cation network that lies approximately in the *ab* plane (Fig. 2) and is best described as a buckled sheet. The network has approximately square channels perpendicular to the sheet (Fig. 2), along the *c* direction, as well as larger channels between sheets, along the *b* direction. The anions sit in the latter channels and interact with the cation network *via* N—H···O (N3) and N—H···π_{CO} (N4) hydrogen bonds (Fig. 1), as well as by very weak C—H···O hydrogen bonds (H···O > 2.65 Å). Thus, three of the seven N—H protons do not form significant hydrogen-bonding interactions (N2—H2*B*, N3—H3*A* and N4—H4*A*) and the tertiary amine site (N1) does not serve as a hydrogen-bond acceptor.

N—H···O hydrogen bonds involving metal–carbonyl acceptor groups (such as N3—H3*A*···O2) are not very common, since hard donor groups such as N—H bonds typically form hydrogen bonds with acceptor groups harder than the relatively soft metal-bound carbonyl. The latter tend to interact more commonly with softer (and more abundant) C—H donors (Braga *et al.*, 1995). N—H···π_{CO} hydrogen bonds are rarer still. To our knowledge, this is the first example discussed in the literature. The assignment as an N—H···π_{CO} hydrogen

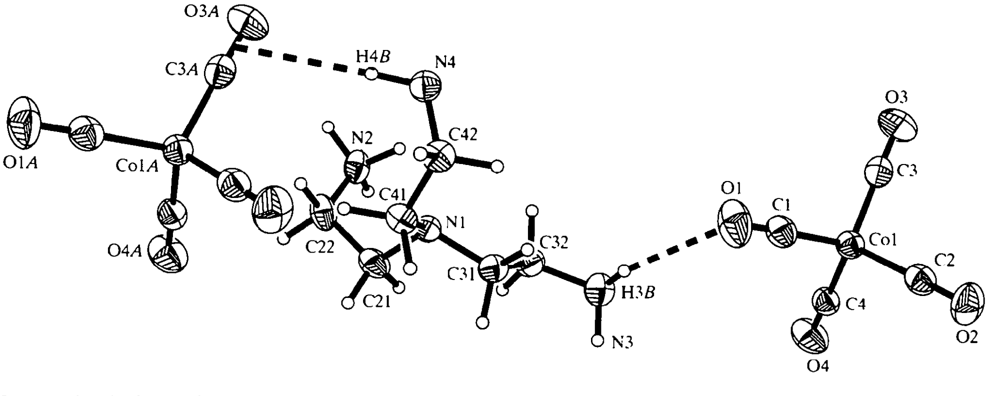


Fig. 1. View of one cation hydrogen bonded to two symmetry-related anions from the crystal structure of $[(tren)H]^+[Co(CO)_4]^-$, (1), showing N—H···O and N—H···π_{CO} hydrogen bonds. Atom labeling is shown, and non-H atoms are represented as 50% probability ellipsoids. Atom H4*A* is hidden behind N4.

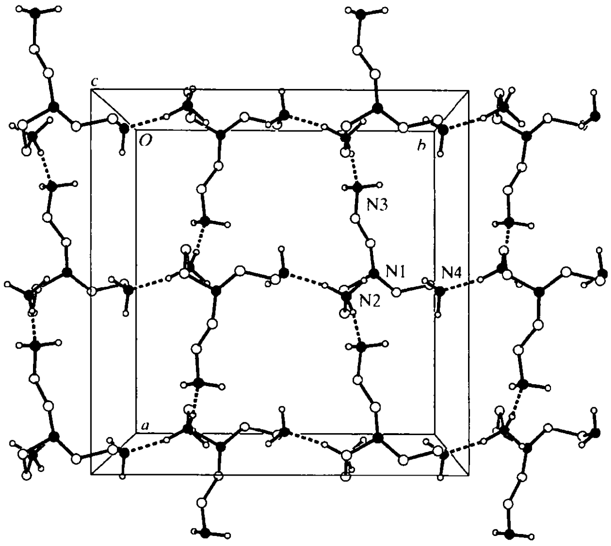


Fig. 2. View down the c axis of the hydrogen-bonded cation grid. N atoms are shaded.

bond rather than an N—H···O hydrogen bond is based upon the acute C≡O···H angle (89.6°, using an N—H distance corrected to the standard 1.01 Å neutron value) and the linearity of the N—H···X angle (X is the C≡O bond midpoint), here 174°. A search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) for both inter- and intramolecular examples of N—H···π_{CO} hydrogen bonds located very few examples (<10), but no attention was drawn to these by the original authors. In contrast, the CSD search identified an appreciable number (a few hundred) of C—H···π_{CO} hydrogen bonds. The uncommon occurrence of N—H···π_{CO} hydrogen bonds can perhaps be rationalized since the π electrons of the C≡O bond can be expected to be a soft-acceptor site for hydrogen bonds (*i.e.* soft base). An article is in preparation on the general topic of D—H···π_{CO} hydrogen bonds (D = C, N, O; Mareque Rivas & Brammer, 1998*d*).

Experimental

The title complex salt, (1), was prepared under an inert argon atmosphere, using standard Schlenk and dry-box techniques, and under the same experimental conditions as those used in the preparation of related salts (Zhao *et al.*, 1996). Thus, the transfer of a hexane solution of HCo(CO)$_4$ to a toluene solution of the tetraamine tren at liquid-nitrogen temperature yielded, upon gentle warming and stirring of the resulting solution, a white precipitate, which was isolated and dried at reduced pressure. Spectroscopic data: ^{1}H NMR (C$_6$D$_5$CD$_3$), 298 K: δ (p.p.m.) 2.20 (*t*), 2.50 (*t*); 183 K: δ (p.p.m.) 2.02 (*t*), 2.41 (*t*); IR (CD$_3$CN solution, cm^{-1}): ν(CO) 1890 (*s*); IR (nujol mull, cm^{-1}): ν(CO) 2007 (*w*), 1921 (*m*), 1898 (*s*), 1869 (*s*). Slow evaporation of a toluene solution of the white precipitate under argon yielded, after several days, colorless crystals of quality suitable to carry out X-ray diffraction studies. The crystal selected for data collection was coated in hydrocarbon oil in an inert atmosphere dry-box. Once outside the dry-box, the oil-coated crystal was quickly glued to a glass fiber mounted on a brass pin and placed under the cold stream of the diffractometer.

Crystal data

(C$_6$H$_{19}$N$_4$)[Co(CO)$_4$]
M_r = 318.22
Orthorhombic
Pbca
a = 13.4327 (2) Å
b = 13.1953 (6) Å
c = 16.7801 (6) Å
V = 2974.2 (2) Å^3
Z = 8
D_x = 1.421 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2.43–30.00°
μ = 1.169 mm^{-1}
T = 208 (2) K
Irregular
0.17 × 0.07 × 0.05 mm
Colorless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1995)
T_{min} = 0.789, T_{max} = 0.943
37 541 measured reflections

2611 independent reflections
1890 reflections with $I > 2\sigma(I)$
R_{int} = 0.100
θ_{max} = 25°
$h = -18 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.055$
S = 1.440
2593 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.265 e Å^{-3}
$\Delta\rho_{min}$ = −0.242 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

Hydrogen-bond geometries were calculated based upon extension of N—H bonds to typical neutron diffraction values; $X3$ denotes the midpoint of the C3≡O3 bond.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N3^{i}	1.01	1.85	2.849 (3)	170
N2—H2C···N4^{ii}	1.01	1.81	2.805 (3)	169
N3—H3B···O1	1.01	2.38	3.217 (3)	139
N4—H4B···$X3^{iii}$	1.01	2.61	3.615 (3)	174

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $-1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x - 1, y, z$.

The absorption correction was based upon symmetry equivalent and repeated intensity measurements using the program *SADABS* (Sheldrick, 1995), which is based upon the method of Blessing (1995). Methylene H atoms were placed in calculated positions and refined using a riding-model constraint. As the site of protonation was unknown prior to crystal structure determination, amine and ammonium H atoms were located from the difference map. These atoms were refined with no positional constraints, but with isotropic displacement parameters constrained to be 1.2 times the equivalent isotropic parameter of the attached N atoms.

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1994*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994*a*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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catena-Poly[[tetrakis(imidazole-N^3)-copper(II)]-μ-(dichromato-O:O')]

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Abstract

The title compound, $[\{Cu(C_3H_4N_2)_4\}(Cr_2O_7)]_n$, containing a $[Cr(Him)_4]^{2+}$ cation (Him = imidazole) and a dichromate anion, was obtained by hydrothermal synthesis. Each Him ligand coordinates to the Cu atom *via* one N atom, forming a tetragonally elongated octahedral geometry with a basal plane defined by four coplanar imidazole N atoms, the axial sites being occupied by O atoms from two dichromato ligands. The dichromate anions bridge the Cu ions to form one-dimensional zigzag chains.

Comment

Complexes of Cu^{2+} and Him with halides have been structurally characterized, such as $[Cu(Him)_4(H_2O)_2)]F_2$, $[Cu(Him)_4]I_2$ and $[Cu(Him)_4]Br_2$ (Vreugdenhil *et al.*, 1984; Akhtar *et al.*, 1968; Ballester *et al.*, 1993; Parker & Breneman, 1995). These molecular structures reveal that the bromide and iodide anions are weakly bound in the axial coordination sites, but in $[Cu(Him)_4(H_2O_2)]F_2$, the fluoride ions are not coordinated to the Cu ion, the fifth and sixth octahedral sites above and below the CuN_4 plane being occupied by two water molecules. The structures of some complexes of oxo acid anions with imidazole–copper(II) have also been reported: $[Cu(Him)_4(SO_4)]$, $[Cu(Him)_4(NO_3)]$ and $[Cu(Him)_4(ClO_4)_2]$ (Fransson & Lundberg, 1972;