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Rudy L. Luck *et al.*

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Tris(1,10-phenanthroline-*N,N'*)-chromium(III) triperchlorate hydrate

Rudy L. Luck,* Paula Gawryszewska and James P. Riehl

Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA

Correspondence e-mail: rluck@mtu.edu

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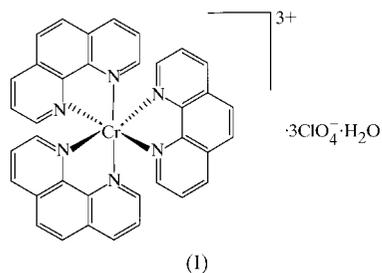
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The structure of the cation in $[\text{Cr}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ consists of the Cr atom bonded to the N atoms of the three 1,10-phenanthroline (phen) ligands, resulting in a distorted octahedral arrangement with the six Cr–N distances ranging from 2.040 (4) to 2.055 (4) Å. One of the perchlorate anions is disordered and is located around two special positions.

Comment

We are interested in the solid-state arrangements of tris(phen)metal (phen is 1,10-phenanthroline) compounds of varying charges complexed with various anionic lanthanide compounds. In the course of this study, crystals of the title compound, (I), were obtained. It is noteworthy that this report represents the first X-ray determined structure of a Cr atom surrounded by three phen ligands, as verified by a search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) which currently lists 43 such studies involving other metals. One of these studies contains isomorphous data for an Fe^{III} analogue, namely $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (Baker *et al.*, 1975). A significant difference between these two structures is that the Cr–N distances [mean 2.05 (1) Å] in the title compound are longer than the Fe–N distances [mean 1.973 (5) Å] in $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. This difference



reproduces the difference in ionic radii (Shannon & Prewitt, 1970) between Cr^{3+} (0.62 Å) and low-spin Fe^{3+} (0.55 Å) in octahedral environments.

The title compound crystallized with one $[\text{Cr}(\text{phen})_3]^{3+}$ cation, two ordered $[\text{ClO}_4]^-$ anions, one $[\text{ClO}_4]^-$ anion arranged around two special positions, and a water molecule constituting the asymmetric unit. There was no evidence of covalent bonding interactions between the perchlorate anions and the cation, however, there are close contacts, probably indicative of hydrogen bonding between the disordered hydrate and O atoms of a perchlorate anion, namely $\text{O50} \cdots \text{O23}$ at 2.72 (1) Å, $\text{O50} \cdots \text{O31}$ at 2.72 (1) Å and $\text{O501} \cdots \text{O23}$ at 2.99 (2) Å, and also between some of the perchlorate O atoms and the surrounding phenanthroline C atoms.

There are no significant differences in the bite angles of the three phenanthroline ligands at 81.3 (2), 81.5 (2) and 81.2 (2)° for angles N1–Cr–N2, N3–Cr–N4 and N5–Cr–N6, respectively. However, there are significant deviations from linearity for the *trans* atoms with angles N1–Cr–N4, N2–Cr–N5 and N3–Cr–N6 at 173.5 (2), 177.5 (2) and 171.2 (2)°, respectively. The rigidity of the phenanthroline ligand has been cited to afford ‘slightly bent metal–ligand bonds’ (Goodwin *et al.*, 1984). Therefore, in this report, the bite angle should not be taken as an indication of distortion with the phen ligand itself. Rather the bite angle appears to correlate well with the metal-to-N-atom distance; 82.6 (4)° and 1.978 (3) Å in $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Koh *et al.*, 1994); 81.0 (2)° and 2.050 (10) Å in this study; 78.1 (3)° and 2.127 (14) Å in $[\text{Co}(\text{phen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Boys *et al.*, 1984); 70.2 (2)° and 2.400 (6) Å in $[\text{Hg}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2$ (Deacon *et al.*, 1979). This can be described by the equation $y = -29.818x + 141.75$, where y represents the bite angle and x is the metal-to-N-atom bond distance.

Finally, it is interesting to note that several structures out of the 43 noted above contain disorder in either the anion or a molecule of hydration. These include $[\text{Cu}(\text{phen})_3](\text{ClO}_4)_2$ (Anderson, 1973), $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (Baker *et al.*, 1975), $[\text{Co}(\text{phen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Boys *et al.*, 1984), $[\text{Os}(\text{phen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Goodwin *et al.*, 1984), $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Koh *et al.*, 1994) and $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6) \cdot 5\text{H}_2\text{O}$ (Freire *et al.*, 1998) for disorder in the anions, and $[\text{Hg}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{EtOH}$ (Deacon *et al.*, 1979) for disorder with the molecules of solvation. Clearly, the larger size of the cations in these molecules compared to the anions results in large vacancies within the crystal lattice for the anions to arrange themselves. This leads to the disordered arrangements.

Experimental

Crystals of the title compound were obtained in an attempt to grow crystals of the mixed-metal compound $[\text{Cr}(\text{phen})_3][\text{Tb}(\text{DPA})_3]$ (DPA is 2,6-pyridinedicarboxylate) by mixing $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_3$ and $\text{Na}_3[\text{Tb}(\text{DPA})_3]$ in H_2O and allowing for slow evaporation of water. The title compound (consisting of a fusion of red–yellow block-like crystals) was produced in addition to an amorphous red material.

Crystal data

[Cr(C₁₂H₈N₂)₃](ClO₄)₃·H₂O
M_r = 908.98
 Monoclinic, C2/c
a = 17.6320 (4) Å
b = 18.2840 (4) Å
c = 22.9980 (4) Å
 β = 91.2700 (14)°
V = 7412.4 (3) Å³
Z = 8

D_x = 1.629 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 47 108 reflections
 θ = 1.02–30.03°
 μ = 0.603 mm⁻¹
T = 100 (2) K
 Fragment, red–yellow
 0.20 × 0.17 × 0.10 mm

Data collection

KappaCCD diffractometer
 φ and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
T_{min} = 0.79, *T_{max}* = 0.94
 47 108 measured reflections
 10 833 independent reflections

4967 reflections with *I* > 2σ(*I*)
R_{int} = 0.049
 θ_{max} = 30.05°
h = -24 → 24
k = -25 → 25
l = -32 → 32

Refinement

Refinement on *F*²
R(*F*) = 0.075
wR(*F*²) = 0.241
S = 1.028
 10 833 reflections
 586 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.1132*P*)²], where
P = (max(*F_o*², 0) + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.14 e Å⁻³
 Δρ_{min} = -0.58 e Å⁻³

The structure was refined first with atoms described with isotropic and then anisotropic displacement parameters to convergence. The disorder of one of the perchlorate ligands was readily apparent and the occupancies at both sites were allowed to refine with their sum constrained to unity. This resulted in final occupancies of 48.6 (2) and 51.4 (2)%. All of the perchlorate ligands were refined with constraints using the *DFIX* option (Sheldrick, 1997) between the Cl and O atoms allowing them to be tetrahedral. In the final cycles of refinement, one O atom (O41) was refined with isotropic displacement parameters. The Cl–O distances were in the range 1.292 (7)–1.463 (5) Å which puts them within the range of distances previously reported for perchlorate ligands (Anderson, 1973; Baker *et al.*, 1975; Boys *et al.*, 1984), some of which were disordered. Additionally, the O atom on the hydrate was split and the occupancies, the sums of which were constrained to unity, were refined with the atoms described with isotropic displacement parameters. Upon convergence, the occupancies were established at the refined values and the atoms then

allowed to refine with anisotropic displacement parameters. H atoms were inserted in calculated positions appropriate for the data collection temperature with isotropic displacement parameters riding on that of the parent C atom. The H atoms on the O atoms modeled as the disordered hydrate were not located or inserted at fixed positions.

Data collection: *KappaCCD Software* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPAK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPAK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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