

Complexation of Secondary Amides to Chromium(III): the X-Ray Structure of a Molecule with Two Modes of Monodentate Organic Amide Co-ordination

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The X-ray crystal structure of the dimer $[\text{Cr}\{\text{H}(\text{chba-Et})\}(\text{py})_2]_2 \cdot 2\text{py}$ [$\text{H}_4(\text{chba-Et}) = 1,2\text{-bis}(3,5\text{-dichloro-2-hydroxybenzamido})\text{ethane}$, py = pyridine] establishes, for the first time, the existence of N-co-ordination of an organic amide to Cr^{III} , the N-atom and carbonyl O-atom of two separate amide groups being co-ordinated to each Cr^{III} centre [Cr-N 2.030(6) and Cr-O 1.976(5) Å]; the potentially tetra-anionic chelating ligand leads to a variety of co-ordination modes.

The co-ordination chemistry of organic amides is an important part of a number of current chemical problems.¹⁻⁵ Of considerable interest is the lowering of reduction potentials of metal couples, *i.e.*, stabilization of high oxidation states, that accompanies N-co-ordination of the organic amide ligand.¹⁻⁴ Our interest in the stabilization of high-valent transition metal complexes has led to an exploration of the co-ordination chemistry of a new ligand, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [$\text{H}_4(\text{chba-Et})$] (1) (Figure 1), with a number of metals. The ligand (1) has been designed to be reasonably resistant to oxidation, to form five- and six-membered chelate rings upon co-ordination, to be easily synthesized and derivatized, and to contain the organic amide ligating functional group. It is well recognized that co-ordination of the organic amide group can occur through the nitrogen atom, the oxygen atom, or both.^{1,5-7} We report here the crystal structure of an unusual chromium(III) dimer in which both possible types of co-ordination are found. This is the first structural example of the nitrogen atom from an organic amide being co-ordinated to a Cr^{III} metal centre.⁸

Chromium trichloride hexahydrate (0.3 g) was added to pyridine (50 ml) and the mixture was heated under reflux until dissolution was complete. 1 equiv. of (1) was added to the boiling chromium-py (py = pyridine) solution, and after 2 min anhydrous sodium carbonate (5 g) was introduced. The mixture was stirred for 2 min and then filtered. Green crystals and a large amount of an amorphous green solid formed on leaving the filtrate in a sealed bottle for several weeks.† A roughly cubic crystal, edge length *ca.* 0.25 mm, was chosen for the X-ray study; oscillation photographs showed a small twin component, but other crystals of suitable size were grossly twinned.

Crystal data: $\text{C}_{22}\text{H}_{18}\text{Cl}_4\text{Cr}_2\text{N}_4\text{O}_8$, $M = 1448.75$, monoclinic, space group $P2_1/c$, $a = 14.343(4)$, $b = 14.225(3)$, $c = 16.447(8)$ Å, $\beta = 104.28(3)^\circ$, $U = 3252(2)$ Å³, $Z = 2$,

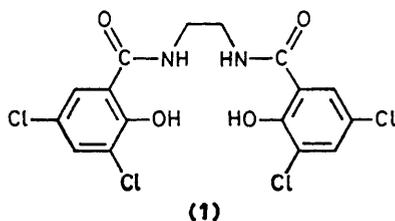


Figure 1. The ligand $\text{H}_4(\text{chba-Et})$, (1).

† Important i.r. spectral data (Nujol, cm^{-1}): 3210 [br., w, $\nu(\text{N-H})$], 1605 (s, sh), 1595 (s, sh), 1580 (sh), 1572 (w, sh), 1550 (br., m), and 1505 (br., s) (spectra identical for both crystalline and amorphous material).

$D_c = 1.48 \text{ g cm}^{-3}$, $\mu = 7.4 \text{ cm}^{-1}$; data (+*h*, ±*k*, ±*l*) were collected on a locally modified Syntex $P2_1$ diffractometer with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å) up to $2\theta = 45^\circ$; a total of 8370 intensity measurements were made with θ - 2θ scans. The three standard reflections, remeasured after each block of 97 reflections, indicated a 5% linear decay over the exposure time of 206 h. The data were corrected for decomposition, but not for absorption; averaging gave 4279 reflections, 3685 with $I > 0$ and 2031 with $I > 3\sigma(I)$.

The positions of the chromium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed in calculated positions and were not refined. The final cycle of refinement gave a goodness-of-fit of 1.38 and $R = 0.122$ ($R_{3\sigma} = 0.055$).‡

The structure consists of discrete dimers and disordered solvent molecules of pyridine. Figure 2 gives bond distances about the Cr centres, which are related by a centre of symmetry. The distorted octahedral environment includes the pyridine nitrogen atoms, an amide nitrogen atom, the phenolic oxygen atoms, and an amide-carbonyl oxygen atom; the co-ordinated pyridine ligands are *cis* and the phenolic oxygen atoms are *trans*.

The carbonyl C-O bond lengths are equal for both co-ordinated and unco-ordinated amide carbonyls 1.278(9) vs. 1.270(9) Å. The Cr-N_{amide} bond length is 2.030(6) Å, and the two Cr-O_{phenol} bond lengths are 1.915(5) and 1.931(5) Å, *cf.*, $[\text{Cr}\{N,N'\text{-ethylenebis}(\text{salicylideneaminato})\}(\text{H}_2\text{O})_2]\text{Cl}$: Cr-N 2.005(9) and 1.997(8) Å, Cr-O 1.916(8) and 1.952(8) Å.⁹ The Cr-O_{carbonyl} bond length is 1.976(5) Å, *cf.*, 1.91(2) Å found in *mer*-trichloro-(*N,N*-dimethylformamide)(1,10-phenanthroline)chromium(III).¹⁰ The Cr-N_{py} bond lengths [2.145(6) Å, *trans*-to-N and 2.097(6) Å, *trans*-to-O] indicate a greater *trans*-influence of the N-co-ordinated vs. the O-co-ordinated amido ligand. The Cr-Cr distance in the dimer is 8.9 Å.

‡ The CRYM computing system was used (D. J. Duchamp, California Institute of Technology). Least-squares refinement minimized $\Sigma w\Delta^2$ with weights $w = \{[\sigma(F^2)]^2 + (0.02 \times \text{scan counts})^2\}^{-1}$ and $\Delta = F_o^2 - (F_c/k)^2$. The goodness-of-fit is $[\Sigma w\Delta^2 / (n-p)]^{1/2}$, $R = \Sigma |F_o - (F_c/k)| / \Sigma F_o$ (for reflections with $I > 0$) and $R_{3\sigma} = R$ [for reflections with $I > 3\sigma(I)$]. The atomic co-ordinates from this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as Supplementary Publication No. SUP 23676 (26 pp.) from the British Library Lending Division. For details of how to obtain this material, see Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3.

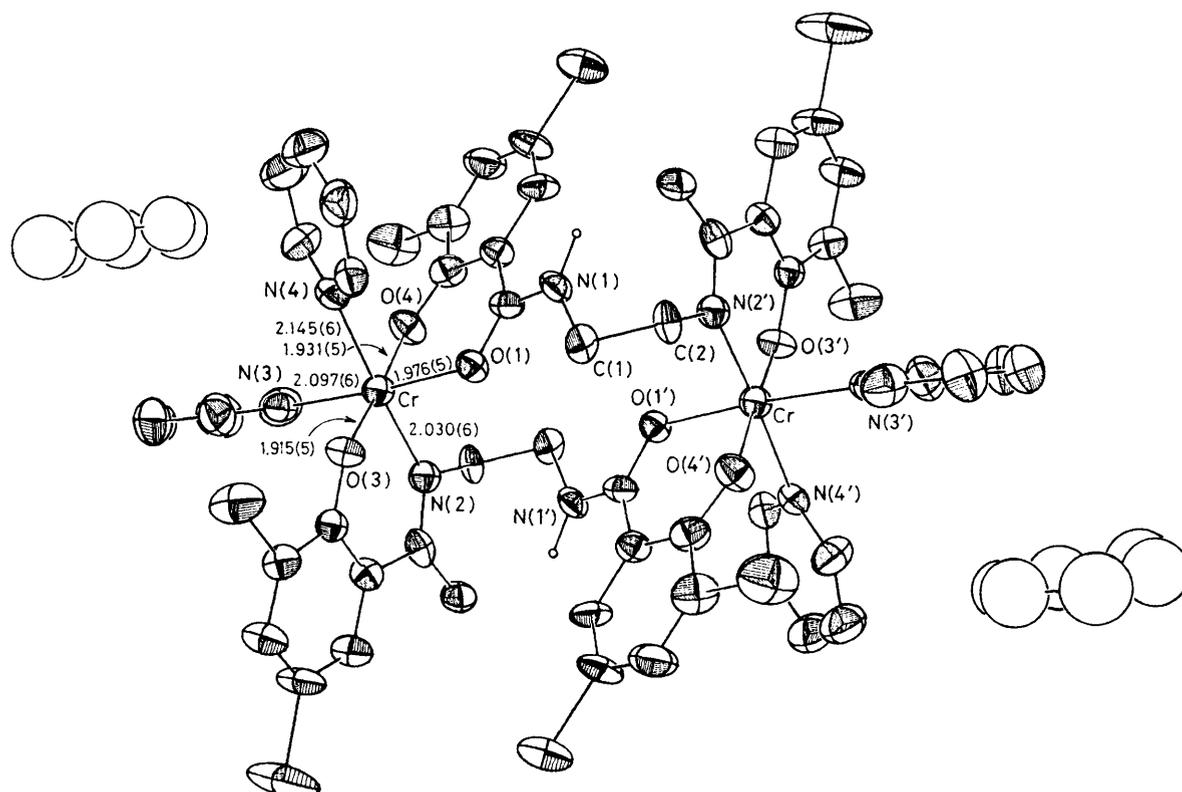


Figure 2. Molecular structure of $[\text{Cr}\{\text{H}(\text{chba-Et})\}(\text{py})_2]_2 \cdot 2\text{py}$.

The ambidentate behaviour of the organic amide functional group is evident, showing that two types of monodentate co-ordination to Cr^{III} are possible, at least where the amide is part of a chelating system. In structural investigations with metals other than Cr, (1) has been found to co-ordinate through the two phenolic oxygen atoms and the two amide nitrogen atoms (all to one metal centre). The strong i.r. band at 1505 cm^{-1} found for the title dimer is not observed in the i.r. spectra of these latter complexes, which exhibit no i.r. bands in the $1500\text{--}1520\text{ cm}^{-1}$ region.

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