Inorganica Chimica Acta
LETTER

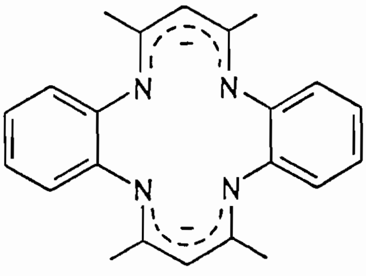
A Five-coordinate, High-spin Chromium(III) Complex: Cr(tmtaa)Cl

F. ALBERT COTTON*, JOANNA CZUCHAJOWSKA, LARRY R. FALVELLO and XEUJUN FENG

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, TX 77843 (U.S.A.)

(Received February 5, 1990)

In practically all known compounds of chromium(III) the chromium atom is found with octahedral coordination. The very few known exceptions are represented by $Cr(NPr_2)_3$ (planar), $Cr(CH_2SiMe_3)_4$ and $CrCl_4^-$ (distorted tetrahedral) and $CrCl_3(NMe_2)_2$ (trigonal bipyramidal) [1]. We are unaware of any example of a five-coordinate chromium(III) complex with square-pyramidal coordination other than the one we report here. The ligand tmtaa is the dianion shown as **I**.



I

An efficient preparation of the compound is by reaction of $CrCl_3$, H_2tmtaa and NEt_3 in a 1:1:2 molar ratio in vigorously refluxing benzene for 24 h. A layer of hexane was placed over the cooled and filtered reaction solution (deep burgundy in color). The product was obtained as large, irregular crystals (nearly 100% yield).

Crystal data for $Cr(C_{22}H_{22}N_4)Cl \cdot C_6H_6 \cdot \frac{1}{2}C_6H_{14}$: triclinic space group $P1$, $a = 13.609(4)$, $b = 16.181(4)$, $c = 12.791(3)$ Å; $\alpha = 107.56(2)°$, $\beta = 115.87(2)°$, $\gamma = 83.95(2)°$; $V = 2415(1)$ Å^3; $Z = 4$; $D_c = 1.516$ g cm^{-3}. A total of 4445 unique data having $2\theta < 45°$ were collected on a Nicolet P3 diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The ω–2θ scan mode was used. Data were corrected for Lorentz and polarization effects** and absorption [2]. The empirical absorption correction made was based on psi scans of several reflections with Eulerian χ angle near 90°. The structure was solved by the Patterson method. The development of the structure was done by alternating sequence of least-squares refinements and difference Fourier maps. All atoms were treated anisotropically, with the exception of the hexane molecule. This hexane molecule resides on an inversion center and was modeled successfully. The final cycle of full-matrix refinement (which was done in two blocks of 383 parameters each) gave $R = 0.0613$ and $R_w = 0.0837$, and quality of fit = 1.839. UV–Vis (THF solution, λ in nm): 770, 720, 620, 530, 458, 416 (shoulder), 394 and 362.

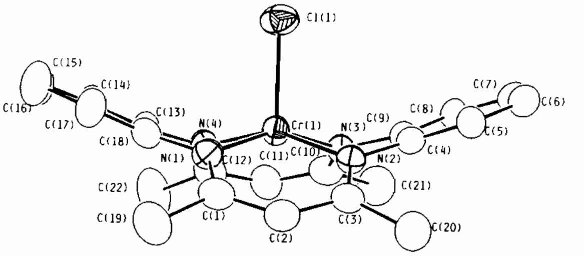


Fig. 1. Side view of the molecule illustrating the saddle shape of the ligand.

The structure of the molecule is shown in Fig. 1. The buckling of the macrocyclic ligand is as expected, and the general shape of the molecule resembles that of Fe(tmtaa)Cl and several similar ones the structures of which have previously been reported [3]. The mean Cr–N distance is 1.971(6) Å, the Cr–Cl distance is 2.250(3) Å and the Cr atom lies 0.435(1) Å above the plane of the four N atoms.

The visible absorption spectrum of the molecule is complicated and cannot be assigned at present (see above). However, the molecule does have three unpaired electrons and that can be understood straightforwardly on the basis of some molecular orbital calculations, as shown in Fig. 2.

The SCF-Xα-SW calculations were done for Cr(tmtaa)Cl and for the Cr(tmtaa) fragment having

---

*Author to whom correspondence should be addressed.

**Calculations were done on a Local Area VaxCluster (VAX/VMS V4.6) with the programs SHELXS-86, SHELX-76 and the commercial package SDP.

0020-1693/90/$3.50

© Elsevier Sequoia/Printed in Switzerland

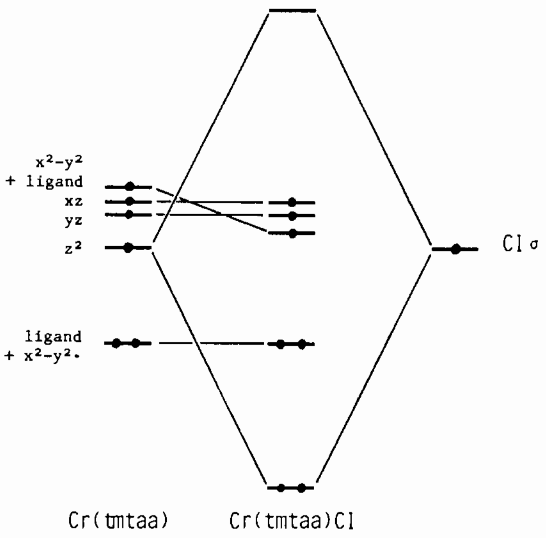


Fig. 2. Molecular orbital diagram for the Cr(III) complex, Cr(tmtaa)Cl.

the same structure as it has in the Cr(tmtaa)Cl molecule. The interaction of this fragment with a chlorine atom leads to the result shown in the center column of Fig. 2. The three unpaired electrons occupy the dπ type orbitals that correspond to the t_{2g} orbitals in an octahedral complex.

Acknowledgement

We thank the U.S. National Science Foundation for support.

References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 680.
2 A. C. T. North, D. C. Philips and T. S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
3 M. C. Weiss, B. Bursten, S.-M. Peng and V. L. Goedkin, *J. Am. Chem. Soc., 98* (1976) 8021.