# Cr(III) Complexes with Thioamides

GARY R. BURNS*, CHRISTINE A. DE ROO,
DAVID W. HALL and ANDREW R. OLIVER

*Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand*

(Received January 21, 1987)

The ability of Cr(III) to coordinate to ligands containing both nitrogen and sulphur donors has not been as well studied as has coordination involving nitrogen and oxygen donor ligands. Indeed the literature is conflicting on the strength of the donor bond formed by the thioketo group in simple thioamides bonded to Cr(III). Thiourea and substituted thioureas have been reported to form complexes with Cr(III) [1, 2] where the ligand is monodentate, coordinated via the thioketo group. The spectrochemical strength of thiourea when bonded to Cr(III) was reported to be particularly low in comparison with its position for thiourea complexes of other transition metals [1]. By contrast, Cr(III) has been reported to form both ionic and neutral complexes with thiosemicarbazide in which the ligand is bidentate, coordinating through both nitrogen and sulphur donor atoms [3]. The spectrochemical strength of thiosemicarbazide bonded to Cr(III) is comparable to the values reported for thiosemicarbazide complexes of other transition metals [4].

We have investigated the ability of Cr(III) to coordinate to the thioamide ligands thiourea (tu) and thiocarbohydrazide (Htcaz), in which nitrogen and sulphur atoms are potential donors. Thiocarbohydrazide has been shown to behave as a bidentate ligand, coordinating to metals via the thioketo group and one of the hydrazinyl nitrogens [4]. This contrasts with thiourea which behaves as a monodentate ligand coordinating to metals via the thioketo group. We report an improved method of preparation for thioamide derivatives of Cr(III), new structural information garnered from spectroscopic and magnetic measurements on the solids and to our knowledge the first coordination compound involving the thioenolic tautomer of thiocarbohydrazide ($tcaz^-$).

## Experimental

Thiocarbohydrazide was prepared as described previously [4], recrystallised from water and dried over $P_4O_{10}$. The starting complex trichlorotris(tetrahydrofuran)chromium(III), $[Cr(THF)_3Cl_3]$ was prepared by the method of Herwig and Zeiss [5]. The thioamide, as a fine powder, was added to the solution containing $[Cr(THF)_3Cl_3]$ and refluxed under a nitrogen atmosphere for approximately one hour. The solution was then decanted and the solvent removed. The mauve complex $[Cr(tu)_3Cl_3]$ was washed repeatedly with hot acetonitrile to remove excess $CrCl_3$ and thiourea. The green–black complex $[Cr(tcaz)_3]\cdot H_2O$ was found to be extremely sensitive to traces of water and to be rapidly solvated by many solvents.

Infrared spectra were recorded as KBr discs and nujol mulls on a Perkin-Elmer Model 599 infrared spectrophotometer. Raman spectra were recorded using a Spex 1401 double monochromator in conjunction with a Spectra Physics Model 164-01 krypton ion laser.

UV–Vis spectra were recorded by reflection using a Unicam SP700 spectrophotometer with $MgCO_3$ as the reference sample. Absorption spectra were recorded for $[Cr(tcaz)_3]\cdot H_2O$ as a nujol mull, in water, tetrahydrofuran and in dimethylsulphoxide using a Perkin-Elmer Model 330 spectrophotometer. Magnetic susceptibilities were measured by the Guoy technique using $[HgCo(NCS)_4]$ as the calibrant.

## Results

Infrared and Raman bands observed for thiourea and $[Cr(tu)_3Cl_3]$ and infrared bands observed for thiocarbohydrazide and $[Cr(tcaz)_3]\cdot H_2O$ are reported in Table I. We were unable to obtain any Raman data for $[Cr(tcaz)_3]\cdot H_2O$ using laser lines from 476 to 647 nm. Electronic data obtained by measuring the visible reflectance spectrum of $[Cr(tu)_3Cl_3]$ and the absorption spectrum of $[Cr(tcaz)_3]\cdot H_2O$ together with room temperature magnetic susceptibilities of both complexes are also listed in Table I.

## Discussion

The visible reflectance data for $[Cr(tu)_3Cl_3]$ is in good agreement with the earlier data of Cervone *et al.* [1]. The absorption spectrum of $[Cr(tcaz)_3]\cdot H_2O$ dispersed in nujol is indicative of a Cr(III) species with a coordination sphere containing 3S and 3N. An estimated value for $\Delta_o$ of *ca.* 18 000 $cm^{-1}$, based on previous measurements on $[Ni(Htcaz)_3Cl_2]$ [4], is in reasonable agreement with the observed data. The absorption spectra of $[Cr(tcaz)_3]\cdot H_2O$ in water ($\tilde{\nu}_1$ = 16 900 $cm^{-1}$), tetrahydrofuran ($\tilde{\nu}_1$ = 16 050 $cm^{-1}$) and dimethylsulphoxide ($\tilde{\nu}_1$ = 15 900 $cm^{-1}$) indicated that solvolysis had occurred. This parallels the

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE I. Infrared, Raman and UV–Vis Spectra ($\tilde{\nu}$ (cm$^{-1}$)) and Magnetic Susceptibilities of Cr(III) Thioamides

| Infrared | | Raman ($\lambda_o$ = 647 mm) | | Infrared | |
|---|---|---|---|---|---|
| tu | $[Cr(tu)_3Cl_3]$ | tu | $[Cr(tu)_3Cl_3]$ | Htcaz | $[Cr(tcaz)_3]\cdot H_2O$ |
| 1617s | 1620s | – | – | 1644s | 1610s |
| | | | | 1622s | |
| 1473s | 1495m | 1477 | 1484 | 1530s | 1550w |
| | 1425s | – | – | – | – |
| 1413 | 1380s | | | 1495m | 1480m |
| – | – | 1374 | – | 1287s | 1290w |
| | 1090m | | | 1142s | 1190s |
| 1086m | 1070sh | 1088 | 1034 | 1080m | 1040s |
| 730s | 720sh | 731 | 713 | 930s | 860s |
| | 695s | | | 755m | 650w |
| 629s | | | | 595s | |
| | 550s,b | 568 | 585 | | |
| 486 | 520sh | 505 | | 476m | 500m |
| | | 480 | | | |
| 463sh,b | 470m | | | | |
| 411m | 432m | | | | |
| – | 330w | | | – | 325m |
| – | 290m | | | | |
| – | 265m | | | | |
| UV–Vis (cm$^{-1}$) | | | | | |
| $^4T_{2g} \leftarrow {}^4A_{2g}$ | | 14350 | | 17300 | |
| $^4T_{1g} \leftarrow {}^4A_{2g}$ | | 19250 | | 23300 | |
| $B$ | | 470 | | 580 | |
| Magnetic susceptibility | | | | | |
| $10^9 \times \chi_g$ (m$^3$ mol$^{-1}$) | | 19.60 | | 23.51 | |
| $\mu_{eff}$ (Bohr magneton) | | 3.83 | | 4.0 | |

behaviour of $[Cr(tu)_3Cl_3]$ where rapid solvolysis has previously been reported [1] to occur in dimethylformamide, dimethylsulphoxide and acetonitrile.

The infrared and Raman data for $[Cr(tu)_3Cl_3]$ have been interpreted using the normal coordinate analysis of Hadzi *et al.* [6]. The infrared active bands assigned to the C–N group at 1473 and 1413 cm$^{-1}$ are raised to 1495, 1425 and 1380 cm$^{-1}$; the NCN deformation mode at 486 cm$^{-1}$ is raised to 550 and 520 cm$^{-1}$; the C=S stretching mode is lowered from 730 to 695 cm$^{-1}$. Similar shifts are observed in the Raman spectrum of $[Cr(tu)_3Cl_3]$, with the band at 1477 cm$^{-1}$ assigned to a C–N mode raised to 1484 cm$^{-1}$ and the band assigned to a C=S stretching mode lowered to 713 cm$^{-1}$. The bands observed in the infrared at 330 and 290 cm$^{-1}$ are assigned as Cr–Cl stretching modes while the band at 265 cm$^{-1}$ is assigned as a Cr–S stretching mode.

The infrared absorption spectrum of $[Cr(tcaz)_3]\cdot H_2O$ has been assigned using the results of a previously published normal coordinate analysis of thiocarbohydrazide [4]. The main changes are large shifts for bands at 1142, 930 and 775 cm$^{-1}$ assigned to normal modes involving the C–N and C=S groups. The changes indicate an increase in the C–N bond order, and a decrease in the C=S bond order greater than those previously reported [4] for the thiocarbohydrazide complexes of the soft acids Cu(II) and Zn(II).

The infrared data for $[Cr(tcaz)_3]\cdot H_2O$ supports the conclusion that the ligand is present as the thioenolic tautomer and that Cr(III) is coordinated via the hydrazinyl nitrogen and the sulphide group. The accompanying shift to lower wavenumber for the amide bands at 1642 and 1622 cm$^{-1}$ parallels that observed for complexes of the thioenolic tautomer of thiosemicarbazide [3, 4].

A feature of the infrared spectra of the Cr(III) thioamides reported here is the significant shift in wavenumber of bands involving C–N and C=S groups. When compared with the shifts observed in the infrared spectra for other metals the shifts for Cr(III) indicate that the Cr–S bond is relatively strong. Any instability can therefore be attributed either to kinetic factors favouring rapid solvation of the Cr(III) complex or to the inherent instability of the ligand.

## References

1 E. Cervone, P. Cancellieri and C. Furlani, *J. Inorg. Nucl. Chem., 30,* 2431 (1968).

2 P. Askalani and R. A. Bailey, *Can. J. Chem., 47,* 2275 (1969).

3 Y. Shibutani, K. Shinra and C. Matsumoto, *J. Inorg. Nucl. Chem., 43,* 1395 (1981).

4 G. R. Burns, *Inorg. Chem., 7,* 277 (1968).

5 W. Herwig and H. H. Zeiss, *J. Org. Chem., 23,* 1404 (1958).

6 D. Hadzi, J. Kidric, Z. V. Knezevic and B. Barlic, *Spectrochim. Acta, Part A, 32,* 693 (1976).