CROATICA CHEMICA ACTA CCACAA **52** (3) 293—298 (1979)

YU ISSN 0011-1643
CCA-1163 546.72
Original Scientific Paper

Metal Complexes of Carbazic Acids IV. Chromium(III) Complexes of *N*-Substituted Carbazic Acids

A. K. Srivastava

Department of Chemistry, Meerut College, Meerut, India

Received January 15, 1979

A series of *N*-substituted carbazic acid complexes of chromium(III) with a general composition CrL_3 (where L = carbazic acid anion, methylcarbazate, phenylcarbazate, 2,3-dimethylcarbazate and 3,3-dimethylcarbazate) was prepared. On the basis of infrared and electronic spectroscopy and magnetism, the structure of these complexes was identified. The ligand field parameters were calculated from the spectral data; the values of IOD_q for the complexes studied are essentially constant, varying only from 17.09 to 18.34 kK*. The values of B in the complexes were reduced very significantly from the free-ion value for chromium(III). The bonding occurs through one of the oxygen atoms of the carboxylate group and amino nitrogen atom.

INTRODUCTION

In order to be able to study the ligational behaviour of *N*-substituted carbazic acids, we did research on the characterization of nickel(II), cobalt(II) and copper(II) complexes of several *N*-substituted carbazic acids, RR′NNR″COOH, as reported in our previous papers[1-3]. These ligands behave as bidentates coordinating the metal ion through one of the oxygen atoms of the carboxylate group and one of the nitrogen atoms[4-6]. In this paper we report the results of our investigation on the coordinating behaviour of carbazate (Cz; $R = R' = R'' = H$), methylcarbazate (MeCz; $R = CH_3$, $R' = R'' = H$), phenylcarbazate (PhCz; $R = C_6H_5$, $R' = R'' = H$), 2,3-dimethylcarbazate (2,3-Me_2Cz; $R = R'' = CH_3$, $R' = H$) and 3,3-dimethylcarbazate (3,3-Me_2Cz; $R = R' = CH_3$, $R'' = H$), towards chromium(III), a metal classified as typically hard. This research was performed in order to further our present knowledge and to fill in some of the gaps in the knowledge of the behaviour of chromium(III) with this class of ligands.

EXPERIMENTAL

Preparation of the Complexes

Tris(carbazate)Chromium(III), $Cr(Cz)_3$. — A slow stream of carbon dioxide was passed into an aqueous solution of hydrazine (6 mmol/dm³), to which, an aqueous solution of chromium(III) chloride was then added. A green-violet coloured compound was immediately obtained, which was filtered, washed successively with small portions of water, ethanol and ether and dried in a vacuum desiccator over phosphorous pentaoxide.

---

* kK = 1000 cm^{-1}

Tris(methylcarbazate)chromium(III), Cr(MeCz)$_3$ and tris(3,3-dimethylcarbazate)-chromium(III), Cr(3,3-Me$_2$Cz)$_3$. — These compounds were obtained by passing a slow stream of carbon dioxide into ethanolic solutions of respective hydrazines and chromium(III) chloride. They could also be prepared by adding chromium(III) chloride solution into previously saturated carbon dioxide solutions of the respective hydrazines. These were filtered and washed with small amounts of ethanol and ether and dried.

Tris(phenylcarbazate)chromium(III), Cr(PhCz)$_3$. — On passing carbon dioxide into an aqueous solution of phenyl hydrazine, a white compound, $C_6H_5NHNHCOOH \cdot C_6H_5NHNH_2$[7] was obtained, which was filtered and dried. The dried product (3 mmol/dm^3) was dissolved in ethanol and added to an ethanolic solution of chromium(III) chloride. A blue compound was immediately obtained, which was collected and washed several times with small portions of ethanol and dried.

Tris(2,3-dimethylcarbazate) chromium(III), Cr(2,3-Me$_2$Cz)$_3$. — An ethanolic solution of *N,N'*-dimethylhydrazine dihydrochloride was neutralized to pH about 7 with an ethanolic solution of KOH. The precipitated KCl was filtered out, and chromium(III) chloride solution in ethanol was then added, and a slow stream of CO_2 was passed when a blue compound slowly separated out, which was collected and washed with small amounts of ethanol and dried.

Analyses and Physical Measurements

Chromium was determined in the complexes by complexometric titration with EDTA using murexide as indicator. Analyses for carbon, hydrogen and nitrogen were performed by micro-analytical methods.

Magnetic measurements were performed on the solid samples with a Guoy balance. HgCo(SCN)$_4$ was used as a calibrant.

The visible reflectance spectra of the finely powdered compounds were recorded on a Beckman DK-2 spectrophotometer fitted with a standard reflectance attachment and magnesium oxide in the reference beam.

Infrared spectra were recorded on a Beckman IR-20 spectrophotometer as a nujol mull or polychlorotrifluoroethylene mull within the range 4000—6000 cm^{-1}.

Analytical data together with magnetic moments are listed in Table I. Electronic spectral bands, their assignments and ligand field parameters are recorded in Table II, and the infrared spectral band positions useful in the diagnostic sense are presented in Table III.

TABLE I

Analytical Data

Compound	Colour	Cr/% Found Calc.	C/% Found Calc.	H/% Found Calc.	N/% Found Calc.	μ_{eff} (BM)
Cr(Cz)$_3$	Blue	18.41 18.77	12.81 12.99	3.32 3.24	30.50 30.52	3.83
Cr(MeCz)$_3$	Violet-blue	16.22 16.31	22.48 22.57	4.78 4.70	26.49 26.33	3.84
Cr(PhCz)$_3$	Blue	10.40 10.27	50.08 49.80	4.19 4.15	16.71 16.60	3.80
Cr(2,3-Me$_2$Cz)$_3$	Blue	14.70 14.40	29.89 29.91	5.85 5.81	23.30 23.26	3.82
Cr(3,3-Me$_2$Cz)$_3$	Blue	14.51 14.40	30.02 29.91	5.78 5.81	23.35 23.26	3.81

TABLE II

Electronic Spectral Data

Compound	ν_1	ν_2	ν_3	10 Dq	B′	β′	λ′
	Observed		Calculated				
$Cr(Cz)_3$	18.18	24.39	36.06	18.18	0.59	0.64	0.047
$Cr(MeCz)_3$	18.34	25.00	37.49	18.34	0.64	0.70	0.036
$Cr(PhCz)_3$	17.09	23.25	34.21	17.09	0.59	0.65	0.077
$Cr(2,3\text{-}Me_2Cz)_3$	17.24	23.25	34.05	17.24	0.57	0.62	0.056
$Cr(3,3\text{-}Me_2Cz)_2$	17.39	23.81	34.60	17.39	0.63	0.69	0.067

TABLE III

Infrared Spectral Bands in cm^{-1}

Compound	ν (NH) or ν (NH_2)	ν_{asy} COO^-	ν_{sym} COO^-	Δ_{COO^-}	ν (N—N)
$H_2NNHCOOC_2H_5$	3340(m) 3300(m)	1720(m) 1630(m)	1450(m)	—	930(m)
$Cr(Cz)_3$	3250(m) 3160(m)	1605(s)	1350(m)	255	990(mbr)
CH_3NHNH_2*	3390(sbr) 3190(ssh)	—	—	—	—
$Cr(MeCz)_3$	3160(mbr)	1600(mbr)	1360(s)	240	1015(wbr)
$C_6H_5NHNHCOOK$	3340(m)	1610(s)	1345(s)	265	1005(w)
$Cr(PhCz)_3$	3280(m) 3200(s)	1590(m)	1370(s)	220	1015(w)
$CH_3NHN(CH_3)COOK$	3180(sbr)	1620(sbr)	1360(s)	260	960(m)
$Cr(2,3\text{-}Me_2Cz)_3$	3100(sbr)	1600(s)	1350(s)	250	960(wbr)
$(CH_3)_2NNHCOONa$	3270(m) 3000(m)	1620(s)	1375(s)	245	1000(w)
$Cr(3,3\text{-}Me_2Cz)_3$	3140(sbr)	1600(s)	1360(s)	240	980(m)

* Ref., U. Anthoni, C. Larsen, and P. H. Nielson, *Acta Chem. Scand.*, 22 (1968) 1025. s = strong; m = medium; w = weak; br = broad; sh = shoulder

RESULTS AND DISCUSSION

Carbazic acid and its mono- and disubstituted derivatives react with chromium(III) to yield blue coloured compounds of the general composition CrL_3 (where L=Cz, MeCz, PhCz, 2,3-Me_2Cz and 3,3-Me_2Cz). It was not possible to crystallise them following their preparation because of the insoluble nature of these compounds. The analytical data, however, indicate that pure compounds were obtained. The insoluble nature of these compounds has further precluded the possibility of determining their coordination geometry in solution. The compounds are fairly stable and can be stored for several months without any apparent change. They do not melt up to 250 ^{0}C.

The magnetic moments and solid state electronic spectra of the complexes reported in this paper agree with those expected for essentially octahedral stereochemistry. The magnetic moment values lie in the range 3.67—3.87 BM, as expected for the three unpaired electrons and these magnetic moments are given by the spin-only term[8].

The absorption spectra of chromium(III) show, in the visible region, two broad but moderately intense bands associated with d-d Laporte-forbidden but also quartet-quartet spin-allowed transitions and are thus, assigned to $^4T_{2g} \leftarrow {}^4A_{2g}$ (F) (ν_1) and $^4T_{1g} \leftarrow {}^4A_{2g}$ (F) (ν_2), respectively. In the near infrared region weak but sharp bands, associated with the doublet-quartet spin-forbidden transitions, were obtained. The third quartet-quartet transition $^4T_{1g}$ (P) $\leftarrow {}^4A_{2g}$ (F) (ν_3) is usually submerged under charge-transfer and inter-ligand transitions in the near ultra-violet region[9] and this appears also to be the case here, although there are indications that ν_3 can be detected in some of the cases but they are not sufficiently resolved to justify listing in Table II. The complexes of chromium(III) with substituted carbazic acids exhibit two major bands in the region 17.09—18.34 kK and 23.25—25.00 kK. The bands' positions are similar to those reported with other oxygen-nitrogen coordinating ligands. One can assign with relative certainty the two bands observed to the ν_1 and ν_2 transitions, respectively. The broadness of ν_1 and ν_2 transitions observed may be due to distortion from octahedral geometry[10]. The most noticeable feature of ν_1 and ν_2 transitions is that the bands are considerably more intense than usual for the octahedral chromium(III) complexes. The enhancement of electronic spectral intensities of these bands may be due to a high degree of covalency and to the lack of symmetry in the complexes[11].

Since the distortion from octahedral structure is small and because there is a lack of supporting detailed spectral data, the spectra have been analysed in terms of a octahedral model, and ligand field parameters Dq and B' have been extracted. In general, the errors arising from this procedure will be small because it appears that small structural distortions have their greatest effect on the intensities of the electronic transitions rather than on the energies of transitions.

The spectra of the complexes yield, by the standard treatment values for the ligand field parameters Dq and B'. The Dq values for the *N*-substituted carbazic acids increase in the order

$$\text{PhCz} < \text{2,3-Me}_2\text{Cz} < \text{3,3-Me}_2\text{Cz} < \text{Cz} < \text{MeCz}$$

which indicates almost equal ligational strength of PhCz, 2,3-Me_2Cz and 3,3-Me_2Cz; Cz and MeCz have almost equal but larger values of Dq. Considering the electron donating potentialities of various substituents in substituted carbazic acids and their respective steric hindrances, the above series is theoretically expected.

The Racah parameter B may be calculated by several methods depending on the transition energies used[12], but, since only ν_1 and ν_2 bands have been observed in the complexes reported only one equation, fitting the second band, has been used to calculate B'. The B' values are of the order of 57—65% of the free ion value and this indicates considerable orbital overlap.

The β' values in our complexes are in the range 0.63—0.70, which is in close agreement with that of other oxygen and nitrogen donor ligands[13].

Using these values of Dq and B', the ν_3 was calculated and presented in Table II.

Assuming the effective octahedral geometry of the complexes, the effective spin-orbit coupling constant, λ', was calculated for the range 36—77 cm^{-1}, and was found to be considerably reduced from the freeion value of 90 cm^{-1}. The order

$$\mathrm{MeCz} > \mathrm{Cz} > 2,3\text{-}\mathrm{Me_2Cz} > 3,3\text{-}\mathrm{Me_2Cz} > \mathrm{PhCz}$$

is understandable in view of the different substituents attached to the carbazic acid.

Infrared Spectra

The carbonyl stretching frequency provides a very important clue to the elucidation of structures. In the formation of the COO^- ion, this is replaced by two bands in the regions 1610—1550 and 1440—1300 cm^{-1}, corresponding respectively to antisymmetric and symmetric stretching vibrations of the carboxylate group[14]. The antisymmetric stretching vibrations of a carboxylate group is known to be particularly sensitive to the mode of coordination. Amino acids and carboxylic acids are known to coordinate through the carboxylate group in which the antisymmetric stretching frequency varies from 1660—1580 cm^{-1} and its value increases with the increase in covalent character of the M—O band.

All the complexes have two absorption bands in the 1600—1590 and 1370—1350 cm^{-1} regions, which have been assigned to the antisymmetric and symmetric COO^- stretching vibrations, respectively.[15] It is known that if only one of the oxygen atoms of the carboxylate group is coordinated to the metal, the antisymmetric frequency of the carboxylate ion would be expected to increase as the vibration assumes a more ketonic character[16]. It has also been established that as the antisymmetric frequency increases, the corresponding symmetric frequency decreases, assuming a more single bond character. The data presented in Table III indicate that $\Delta\, COO^-$ in the complexes reported is of the same order of magnitude as is reported[17] for a series of amino acid complexes.

It is apparent from Table III that almost all the absorption bands observed above 3000 cm^{-1}, assigned to NH or NH_2 stretching vibrations, are shifted to lower wave numbers in the complexes. The major cause for this lowering[18–20] is the drainage of electrons from the nitrogen atom, which in turn weakens the N—H bond. This clearly indicates the coordination of the nitrogen atom to chromium(III).

The N—N stretching vibration has been assigned to a band observed in the 1015—960 cm^{-1} region. The distinction between chelated and nonchelated carbazic acids has been made[5] only by the broadening of the N—N stretching band in the chelates. The slightly broad character of this band in our complexes may be taken as evidence for the nitrogen involvement in the bond formation.

N(3) is assumed to be coordinated to the metal in Cz and MeCz complexes, while this nitrogen attached to the phenyl group in PhCz, should be electronically incapable of bond formation; hence N(2) is believed to be involved in the coordination to chromium(III) in its complex. In 2,3-Me_2Cz complex

N(3) coordination is again assumed in agreement with the enhancement of Lewis basicity by a methyl group on the atom N(3). The very similar ligand MeNHN(Me)CSS$^-$ is coordinated through the N(3) atom to nickel(II)[21]. In 3,3-Me$_2$Cz the inductive effect of the methyl groups would be expected to enhance the Lewis basicity of the adjacent nitrogen atom[22]. Moreover, the appearance of a band in the 2820—2760 cm^{-1} region, in compounds containing a =N(CH$_3$) group, has been correlated[23] with the presence of an unshared electron pair in the nitrogen atom. Hence, this band is expected to disappear upon coordination of this nitrogen to the metal ion. The absence of a band in this region in the 3,3-Me$_2$Cz complex further indicates the coordination of N(3) in this complex.

REFERENCES

1. A. K. Srivastava and F. Tarli, *J. Inorg. Nucl. Chem.* **39** (1977) 1793.
2. A. K. Srivastava, *Trans. Met. Chem.* (in press).
3. A. K. Srivastava, Communicated.
4. A. Braibanti, G. Bigliardi, A. M. M. Lanfredi, and A. Tiripicchio, *Nature,* (1960) 1175.
5. A. Braibanti, A. Tiripicchio, A. M. M. Lanfredi, and M. Camellini, *Acta Crystallogr.* **23** (1967) 248.
6. A. Braibanti, F. Dallavalle, M. A. Pellinghelli, and F. Leporati, *Inorg. Chem.* **7** (1968) 1430.
7. A. Stern, *J. Prakt. Chem.,* **60** (1899) 236.
8. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.,* **6** (1964) 102.
9. A. B. P. Lever, *Inorganic Electronic Spectroscopy, Elsevier,* Amsterdam (1968).
10. R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.* **10** (1971) 2710.
11. C. K. Jorgensen, *J. Inorg. Nucl. Chem.* **24** (1962) 1571.
12. E. Konig, *Inorg. Chem.,* **10** (1971) 2632.
13. C. Preti and G. Tosi, *Canad. J. Chem.,* **52** (1974) 2845.
14. L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Methuen, London, 1964.
15. A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.* (1962) 5262.
16. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* pp. 223, 233, Wiley N. Y., 1963.
17. K. Ho. and J. J. Zuckerman, *Inorg. Chem.* **12** (1973) 1552.
18. J. Chatt, L. A. Ducanson, and L. M. Venanzi, *J. Chem. Soc.* (1955) 4461.
19. J. Chatt, L. A. Ducanson, and L. M. Venanzi, *J. Chem. Soc.,* (1956) 2712.
20. G. F. Svato, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.,* **77** (1955) 6159.
21. L. Gastaldi and P. Porta, *Cryst. Struct. Comm.* **4** (1975) 693.
22. R. F. Evans and W. Kynaston, *J. Chem. Soc.,* (1963) 3151.
23. J. F. Braunholtz, E. Ebsworth, F. Mann, and N. Sheppard, *J. Chem. Soc.* (1958) 2780.

SAŽETAK

Kovinski kompleksi karbazinskih kiselina IV. Kromovi kompleksi *N*-supstituiranih karbazinskih kiselina

A. K. Srivastava

Pripravljeni su kompleksi kroma sa metilkarbazatom, fenilkarbazatom, 2,3-dimetilkarbazatom i 3,3-dimetilkarbazatom. U radu se raspravlja o fizičko-kemijskim karakteristikama sintetiziranih spojeva na temelju spektroskopskih podataka.

DEPARTMENT OF CHEMISTRY
MEERUT, COLLEGE
MEERUT, INDIA

Prispjelo 15. siječnja 1979.