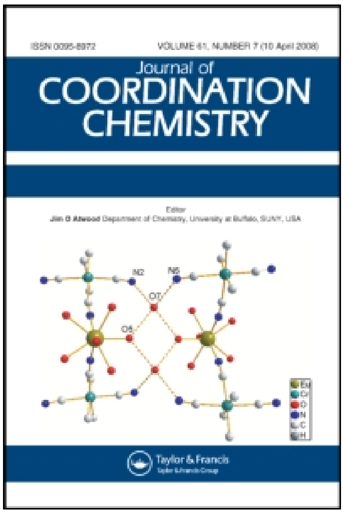

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THE CRYSTAL AND MOLECULAR STRUCTURE OF RUBIDIUM BIS(PYRIDINE-2,6-DICARBOXYLATO)-CHROMATE(III)

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THE CRYSTAL AND MOLECULAR STRUCTURE OF RUBIDIUM BIS(PYRIDINE-2,6-DICARBOXYLATO)-CHROMATE(III)

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A three dimensional X-ray structural analysis of rubidium bis (pyridine-2,6-dicarboxylato)chromate(III), Rb[Cr(dipic)$_2$], has been carried out. The structure was refined by full matrix least-squares methods, using 713 observed independent reflections recorded at room temperature, to a conventional weighted R of 0.034. The crystals are tetragonal with a = b = 6.950(3) Å, c = 29.47(1) Å, space group I4$_1$/a and Z = 4. The point group symmetry of the [Cr(dipic)$_2$]$^-$ ion is S$_4$. The Cr–N and Cr–O distances (1.974(4) and 2.000(3) Å respectively) noticeably differ from the usual values in aminoacid chromium(III) complexes. The π bonding effect of the pyridine nitrogen atom corroborates the previous spectral studies on the sodium salt of this complex. The lability of [Cr(dipic)$_2$]$^-$ in acid solution has been tentatively explained on the basis of the relatively severe strain within the complex ion.

INTRODUCTION

As part of a systematic study of chromium(III) complexes with aminoacids, we have investigated the pyridine-2,6-dicarboxylic acid (H$_2$ dipic)/chromium(III) system. [Cr(dipic)$_2$]$^-$ was found to be by for more labile than the analogous complexes formed with iminodiacetic acid (H$_2$ida), methyliminodiacetic acid (H$_2$mida) and cis-piperidine-2,6-dicarboxylic acid (H$_2$dipicred). Difference in reactivity might reflect difference in stereochemistry, thus a crystallographic study of these complexes was undertaken.

We report here the crystal structure of Rb[Cr(dipic)$_2$]. The crystals of the sodium salt Na[Cr(dipic)$_2$]·2.5 H$_2$O which were investigated first, were found twinned and thus unsuitable for an X-ray structural determination.

When this work was started, the only reported structure of a chromium(III) complex with an aminoacid was that of tris(glycinato)chromium(III) monohydrate, [Cr(gly)$_3$]·H$_2$O.[1] Very recently a preliminary report of the crystal structures of three chromium(III) complexes with iminodiacetic acid, K[Cr(ida)$_2$]·3H$_2$O, *i*-propyliminodiacetic acid, Na[Cr(*i*-pida)$_2$]·2H$_2$O, and *t*-butyliminodiacetic acid, K[Cr(*t*-bida)$_2$]·4H$_2$O, has appeared.[2]
In connection with the present study, the recent report of the crystal structure of μ-dihydroxo-bis-[pyridine-2,6-dicarboxylatoaquachromium(III)] [Cr(dipic)(OH)(H$_2$O)]$_2$ is also of interest.[3]
More than twenty structures of complexes with pyridine-2,6-dicarboxylic acid had been previously reported.[4-21] Interest in these compounds arises from the versatile behaviour of the ligand which can bind as dipic^{2-}, Hdipic$^-$ [11,12] or H$_2$dipic[10,14] and from its ability to promote uncommon stereochemistries.[21]

EXPERIMENTAL

Preparation of the Complexes

The sodium salt of [Cr(dipic)$_2$]$^-$ was prepared as previously described[22] Chemical analysis as well as thermogravimetric study led to formulate this compound as a 2.5 hydrate rather than a 1.5 hydrate as previously reported.[22] Crystals of the rubidium salt Rb[Cr(dipic)$_2$] were obtained by adding rubidium chloride to a *ca.* 0.03M solution of the sodium salt, followed by slow evaporation at room temperature.

X-ray Studies

Preliminary crystallographic data were obtained by the precession method, using MoKα radiation (0.71069 Å). Lattice constants were obtained from films micrometering and diffractometer alignments: a = b = 6.950(3)Å; c = 29.47(1)Å.

Systematic extinction, $h + k + l = 2n+1$ for all reflections, $h = 2n+1$ for $h\ k\ 0$ and $l = 4n+1$ for $00l$ correspond to the space group $I4_1/a$. The computed density of 2.18 g.cm^{-3} assuming four formula units per unit cell agrees with the experimental density of 2.17 g.cm^{-3} measured by the flotation method in a mixture of methyliodide and ethyliodide.

An anvil-shaped crystal (0.26 x 0.26 x 0.28 mm) was used for data collection. The crystal was mounted on a glass fiber with the $00l$ axis parallel to the fiber axis and aligned parallel to the ϕ axis of an automatic four-circle diffractometer. MoKα radiation was used. Intensities were measured at room temperature with a scintillation counter and a pulse height analyser set on MoKα energy in such a way that 90% of the diffracted intensity was collected. A graphite monochromator was set in front of the counter window. The crystal-focus and crystal-counter distances were 23 cm.

843 independent reflections with $\theta < 26.25°$ were collected, of which 713 were considered as observed. The $\theta-2\theta$ scan was used with a sweep of 1.2° at zero Bragg angle and a rate of 2.25°min^{-1}; the Kα_1–Kα_2 dispersion was taken into account. Background intensity was measured during 6.7 sec before and after each scan, in fixed positions. Three standard reflections, 400, 040 and 0016, were recorded every 50 reflections and no significant decrease in intensity during the course of the experiment was observed. All intensities were corrected for counting losses[23] and for Lorenz and polarization effects.

For each reflection, the statistical error on observed intensity was computed as: $\mathrm{ERR} = [\mathrm{Iobs} + \mathrm{CORPER} + \mathrm{FC(BAL/TFC)}^2]^{1/2}$ were Iobs is the observed intensity, CORPER is the counting loss, FC is the background count, BAL and TFC are the times for scan and background measurements.
A reflection was taken as observed if $\mathrm{Iobs} + \mathrm{CORPER} - \mathrm{FC(BAL/TFC)} > \mathrm{ERR}$. The standard deviation was taken as $\sigma = \mathrm{ERR}/2F$, F being the structure factor, for observed reflections and $\sigma = (\mathrm{ERR}/3)^{1/2}$ for null reflections.

Atomic parameters have been refined using a full matrix least-squares program, minimizing the quantity $\Sigma w^2(|Fo|-|Fc|)^2$ where Fo and Fc are the observed and calculated structure factors put on the same scale, and w is the weight taken as $1/\sigma$.
R factors are defined as:

$$R = \frac{\Sigma||Fo|-|Fc||}{\Sigma|Fo|} \quad \text{and}$$

$$R_w = \left[\frac{\Sigma w^2(|Fo|-|Fc|)^2}{\Sigma w^2|Fo|^2}\right]^{1/2}$$

Atomic scattering factors for Cr,N,C,O,H and Rb$^+$ were corrected for the real and imaginary parts of anomalous dispersion.[24] Attempts to use scattering factors for Cr^{3+} and O$^-$, for those of the oxygen atoms which are bound to the chromium ion, instead of those for Cr and O did not lead to any significant change.

Solution and Refinement of the Structure

Since the cell contains four formula units, the four chromium atoms and the four rubidium atoms are on special a and b positions. A structure factor calculation based upon this led to $R_w = 0.37$. As the chromium ion lies on the $\bar{4}$ axis, only the N,C_1,C_2-C_3,C_4,O_1 and O_2 atoms have to be located (see Figure 1 for numbering). Moreover, both N and C_4 lie on special e positions. Approximate Cr–N and N–C_4 distances of about 2.0 and 2.75 Å respectively were introduced into the calculation on the basis of the previous reported copper[10] and nickel[11] structures. Refinement of N and C_4 z-coordinates led to $R_w = 0.35$. At this stage, a three-dimensional Fourier map revealed all remaining nonhydrogen atoms. Refinement led to $R_w = 0.047$. Introduction of calculated pyridine hydrogen positions into the refinement, with anisotropic thermal parameters taken equal to those of the carbon atoms to which hydrogen atoms are bound, dropped R_w to 0.044. Anisotropic thermal parameters were then assumed for all atoms and led to $R_w = 0.035$. Attempt to correct data for absorption did not improve the final R; the linear absorption coefficient was 46 cm^{-1} and the transmission coefficient ranged from 0.448 to 0.471.

The final R factors are:

R	including zeros	0.050
R	excluding zeros	0.039
R_w	including zeros	0.035
R_w	excluding zeros	0.034

Spectral Measurements

The IR spectra were recorded on a Beckman IR – 12 spectrophotometer or a Perkin-Elmer 283 spectrophotometer as potassium bromide or caesium iodide pellets from 4000 to 200 cm^{-1}. The compounds were also studied on a Grubb-Parsons Cube MK-II interferometer as polyethylene pellets from 350 to 50 cm^{-1}.

TABLE I
Final atomic fractional[a] and thermal[b] parameters with estimated standard deviations in parentheses

Atome	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rb	0	2500	6250	3.00(2)	3.00(2)	2.59(3)	0.0	0.0	0.0
Cr	0	2500	1250	1.87(3)	1.87(3)	1.68(4)	0.0	0.0	0.0
N	0	2500	580(1)	1.92(2)	1.63(2)	1.98(1)	−0.1(2)	0.0	0.0
O_1	2553(4)	1290(4)	1119.9(8)	2.3(1)	2.7(1)	2.3(1)	0.3(1)	−0.1(1)	0.0(1)
O_2	4494(4)	316(4)	563.3(9)	2.4(1)	3.2(1)	3.2(1)	0.7(1)	0.2(1)	−0.1(1)
C_1	3041(5)	1100(5)	697(1)	1.9(1)	1.8(1)	2.5(1)	−0.1(1)	0.2(1)	−0.1(1)
C_2	1549(5)	1854(5)	363(1)	2.0(1)	1.4(1)	2.5(1)	−0.2(1)	0.4(1)	−0.2(1)
C_3	1602(6)	1848(6)	9896(1)	2.7(2)	1.9(1)	2.3(1)	−0.2(1)	0.4(1)	−0.1(1)
H_3	257(8)	131(8)	979(2)						
C_4	0	2500	9663(2)	3.5(3)	2.5(3)	2.1(2)	−0.1(3)	0.0	0.0
H_4	0	250	933(2)						

[a] Fractional coordinates × 10^4 (hydrogen atom coordinates × 10^3)
[b] Anisotropic thermal parameters (Å^2) in the form:

$$\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$$

the anisotropic thermal parameters of the hydrogen atoms H_3 and H_4 are equal to those of the carbon atoms C_3 and C_4.

TABLE II
Interatomic distances and angles

Distances, Å

Cr–N	1.974(4)	C_1–C_2	1.523(5)
Cr–O_1	2.000(3)	C_2–C_3	1.376(5)
C_1–O_1	1.298(4)	C_3–C_4	1.386(5)
C_1–O_2	1.214(4)	C_3–H_3	0.84(6)
C_2–N	1.330(4)	C_4–H_4	0.99(7)

Angles, deg.

N–Cr–O_1	78.95(7)
C_2–N–C'_2	122.5(4)
Cr–N–C_2	118.7(2)
Cr–O_1–C_1	117.3(2)
C_2–C_1–O_1	114.1(3)
C_2–C_1–O_2	120.7(3)
O_1–C_1–O_2	125.1(3)
N–C_2–C_3	120.2(4)
N–C_2–C_1	110.9(3)
C_1–C_2–C_3	128.8(3)
C_2–C_3–C_4	118.3(4)
C_2–C_3–H_3	114(3)
C_4–C_3–H_3	127(3)
C_3–C_4–C'_3	120.3(5)
C_3–C_4–H_4	119.8(2)

RESULTS AND DISCUSSION

Positional and anisotropic thermal parameters with their estimated standard deviations are given in Table I. Bond lengths and angles are given in Table II†. ORTEP drawings[25] are shown in Figures 1 and 2.

Coordination of the Chromium Ion

As expected, the complex anion has a trans meridional structure; each ligand is bound through its nitrogen atom and two oxygen atoms. The point group symmetry of $[Cr(dipic)_2]^-$ is S_4. The chromium coordination octahedron is distorted: the chelation angle, N–Cr–O_1, is only 78.9° so that the four coordinated oxygen atoms do not lie in a plane containing the chromium ion. The decrease in the chelation angle with respect to that found in $[Cr(gly)_3]\cdot H_2O$ (81.7°)[1] presumably reflects the greater rigidity of dipicolinate compared to glycinate.

Cr–N and Cr–O_1 distances are equal to 1.974(4) and 2.000(3) Å respectively; they are nearly identical to those found in $[Cr(dipic)(OH)(H_2O)]_2$,[3] and are compared in Table III to other Cr–N and Cr–O distances found in various complexes. It appears that Cr–N distance in $[Cr(dipic)_2]^-$ is significantly shorter than the value of 2.07 Å which can be considered as the normal Cr–N bond length, while the Cr–O distance is appreciably longer than the normal value for a Cr–O bond length. Although the structure of $Na[Cr(dipicred)_2]\cdot 3H_2O$ is not

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†A table of observed and calculated structure factors is available from the Editor upon request.

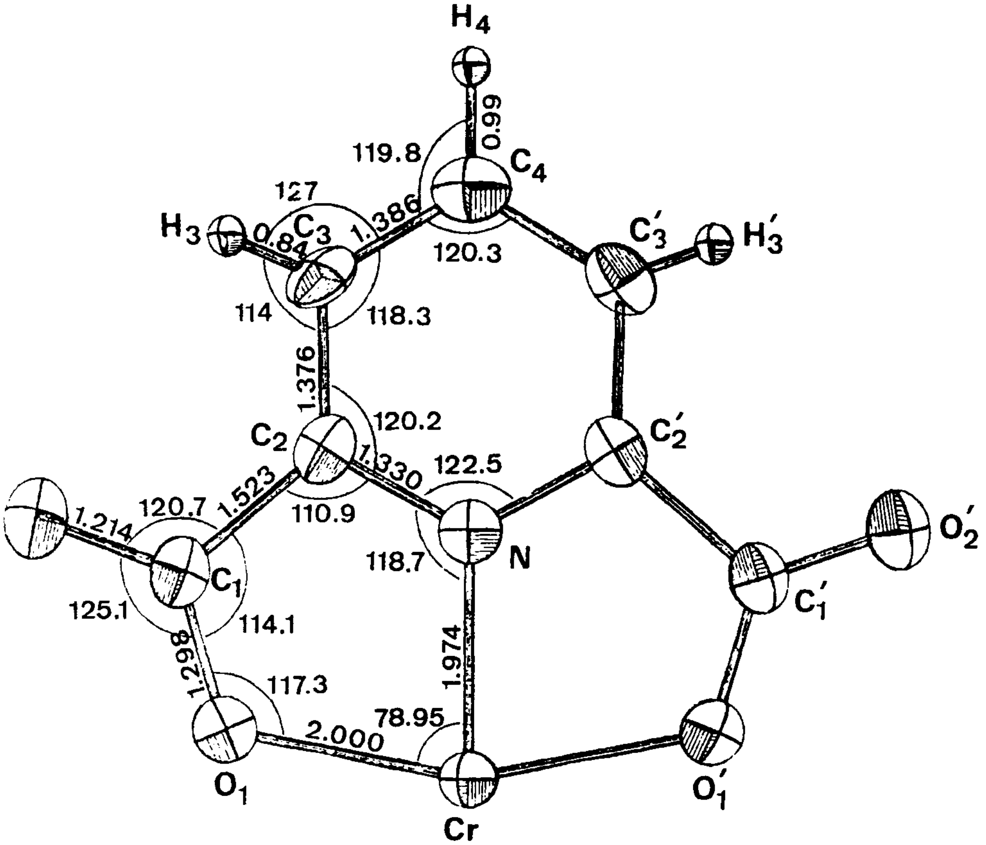

FIGURE 1 ORTEP drawing of half the $[Cr(dipic)_2]^-$ ion with the labelling scheme and distances and angles. Thermal ellipsoids are shown at the 50% probability level (hydrogen atoms are drawn with dummy ellipsoids).

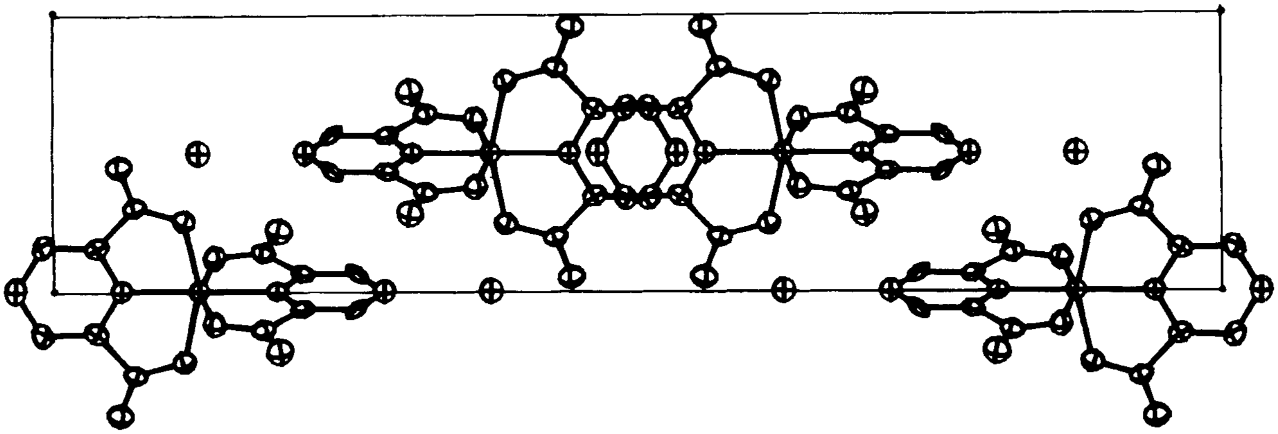

FIGURE 2 ORTEP view down the b axis showing molecular packing. Thermal ellipsoids are shown at the 50% probability level.

TABLE III
Mean Cr–N and Cr–O bond lengths in some chromium(III) complexes

Compound[a]	Cr–N (Å)	Cr–O (Å)	Reference
$Rb[Cr(dipic)_2]$	1.974	2.000	This work
$Na[Cr(dipicred)_2]\cdot 3H_2O$	2.053	1.958	26
$Na[Cr(i\text{-}pida)_2]\cdot 2H_2O$	2.118	1.964	2
$K[Cr(t\text{-}bida)_2]\cdot 4H_2O$	2.152	1.963	2
$K[Cr(ida)_2]\cdot 3H_2O$	2.070	1.961	2
$[Cr(gly)_3]\cdot H_2O$	2.068	1.965	1
$[Cr(NH_3)_6][CuCl_5]$	2.064		27
$\pm[Cr(en)_3]Cl_3$	2.079		28
$K_3[Cr(ox)_3]\cdot 3H_2O$		1.951	29
$Cr(acac)_3$		1.90	30

[a] en = ethylenediamine; ox = oxalate; acac = acetylacetonate; other symbols have been already defined.

completely solved, preliminary results show that dipicred^{2-} adopts a facial configuration around chromium and that the Cr–N and Cr–O distances lie in the normal range.[26] The somewhat longer Cr–N distances found in $Na[Cr(i\text{-}pida)_2]\cdot 2H_2O$ and $K[Cr(t\text{-}bida)_2]\cdot 4H_2O$,[2] have been ascribed to the increased steric hindrance around the nitrogen atom.[34]

The shortening of the M–N bond and the lengthening of the M–O bond are also observed when dipicolinato complexes of copper[6,9] and nickel[13] are compared to their glycinato analogues.[31,32] However, the effect does not occur for picolinato complexes which have normal M–N and M–O bond lengths.[33] This points to the fact that dipicolinate must be forced to achieve tridentate meridional coordination.

The shortening of the Cr–N bond in $[Cr(dipic)_2]^-$ brings direct evidence for the interaction between the metal t_{2g} electrons and the π-system of the pyridine ring. Such an interaction has been already postulated in view of the large number of vibronic bands, including internal vibrations of the pyridine ring, which have been found in luminescence and absorption spectra of $Na[Cr(dipic)_2]\cdot 1.5H_2O$.[35] The π-bonding effect of the pyridine nitrogen atom is also consistent with the low Dt-value of about 100 cm^{-1} assumed in $Na[Cr(dipic)_2]\cdot 1.5H_2O$.[36]

Geometry of the Ligand Molecule

Bond lengths and angles in the ligand are close to those observed in the free ligand[37] and in other dipicolinato complexes. The two C–O distances within the carboxylate group (C_1–O_1 = 1.298 Å and C_1–O_2 = 1.214 Å) compare well to those found in

TABLE IV
Equations of least-squares mean planes through selected groups of atoms

Atoms	Plane	Equation
N,C_2,C_3,C_4,C'_3,C'_2	1	0.3807 x + 0.9247 y = 1.6067
Cr,N,C_2,C_1,O_1	2	0.4224 x + 0.9062 y = 1.6226

Distances of atoms from these planes (in Å)

Atom		Cr	C_1	O_1	O_2	N	C_2	C_3	C_4	C'_3	C'_2
Plane	No 1	0.000	0.093	0.102	0.214	0.000	0.005	–0.005	0.000	0.005	–0.005
	No 2	0.012	0.003	0.007	0.077	0.020	–0.017	–0.007	0.064	0.113	0.079

$[Cr(gly)_3]\cdot H_2O$,[1] in spite of the fact that the Cr–O bond is longer in $Rb[Cr(dipic)_2]$ than in $[Cr(gly)_3]\cdot H_2O$, what was expected to lead to a more ionic Cr–O bond and consequently to a more symmetrical carboxylate group in $[Cr(dipic)_2]^-$.

The C_1–C_2–N angle is of special interest since its variation shows the ligand deformation with coordination. The value for $Rb(Cr(dipic)_2]$ (110.9°) compares well to those found in $[Cr(dipic)(OH)(H_2O)]_2$ (112.5°)[3] and in dipicolinato complexes of copper and nickel but is significantly lower than those of the free ligand (115.3 and 118.4°).[37] It is worth pointing out that the decrease in the C_1–C_2–N angle with coordination is greater for dipicolinate than for picolinate.

The equations of the least-squares mean planes through the pyridine ring and the chelate ring are given in Table IV. The pyridine ring is planar within experimental errors but the chelate ring shows some departure from planarity. The angle between the two mean planes is 2.8°. The deviation of the ligand from planarity is believed to result from strain within the complex. Such strain is also evidenced by the low overall thermal vibration.

Infrared and Raman Studies

The IR spectrum of $Na[Cr(dipic)_2]\cdot 1.5H_2O$ has been previously reported to 250 cm^{-1} by Hoggard and Schmidtke.[22] The strong coupling to a 213 cm^{-1} frequency in the luminescence spectrum of $Na[Cr(dipic)_2]\cdot 1.5H_2O$ led these authors to predict that a 213 cm^{-1} line should also appear in the IR spectrum. We have now recorded the IR spectrum of $Na[Cr(dipic)_2]\cdot 1.5H_2O$ down to 50 cm^{-1} and indeed we have found a weak band at 215 cm^{-1}. Furthermore we have recorded the IR spectrum of $Rb[Cr(dipic)_2]$ from 4000 to 50 cm^{-1}. The spectra of both salts are very similar above 200 cm^{-1} except for the occurrence of some additional bonds near 3500, 1650 and 550 cm^{-1} in the spectrum of the sodium salt; they are obviously due to lattice water. The 361 cm^{-1} band in the spectrum of the sodium salt has been previously assigned to the Cr–N stretching mode.[22] The assignment is supported by the occurrence of a weak line at 354 cm^{-1} in the Raman spectrum of $Na[Cr(dipic)_2]\cdot 1.5H_2O$,[22] and of a band at 335 cm^{-1} in the IR spectrum of $Na[Cr(dipicred)_2]\cdot 3H_2O$,[26] the shift to lower frequency being consistent with the longer Cr–N distance in $Na[Cr(dipicred)_2]\cdot 3H_2O$ compared to $Rb[Cr(dipic)_2]$.

CONCLUSION

The determination of the crystal and molecular structure of $Rb[Cr(dipic)_2]$ can be correlated to some chemical properties of the $[Cr(dipic)_2]^-$ ion. The shortening, hence the strengthening, of the Cr–N bond presumably results in an increase in the complex stability. No reliable data are available about the stability of chromium(III) complexes of dipicolinic acid and other related tridentate ligands. However it may be noticed that the stability of dipicolinato complexes with most divalent metal ions is greater than expected with respect to the lower basicity of the pyridine nitrogen atom compared to the aliphatic nitrogen atom of iminoacetic acid.[38] However, the possible increase in the $[Cr(dipic)_2]^-$ stability occurs with relatively severe strain within the complex: the actual Cr–N and Cr–O distances are not those which would have been observed in the absence of strain. This could be responsible for the greater lability of $[Cr(dipic)_2]^-$ compared to $[Cr(mida)_2]^-$and $[Cr(dipicred)_2]^-$. The acid aquation of $[Cr(dipic)_2]^-$was found[26] to proceed in three steps, the first of which, with an acid-independent rate constant of 92 sec^{-1} at 20°C and ionic strength 2.0 (perchloric acid-sodium perchlorate mixtures) has no counterpart in the acid aquation of $[Cr(mida)_2]^-$,[39] and $[Cr(dipicred)_2]^-$.[26]

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