Synthesis and Structure of *cis*-Dichlorobis(2-phenylazopyridine)chromium(II), an Inert Chromium(II) Compound*

VIRGINIA FERREIRA, RONALD A. KRAUSE**

Department of Chemistry, University of Connecticut, Storrs, Conn. 06268, U.S.A.

and SINE LARSEN

Department of Physical Chemistry, H. C. Ørsted Institute, Copenhagen, Denmark

(Received July 28, 1987)

Abstract

Recent studies have shown 2-phenylazopyridine (Azpy) to be a useful departure from polypyridyl type ligands in coordination chemistry; frequently lower oxidation states are stabilized by this ligand. We have prepared and studied $[Cr(Azpy)_2Cl_2]$ which is surprisingly inert for a chromium(II) complex. The compound crystallizes in the space group $P2_1/c$ with $a = 7.953(3)$, $b = 21.189(11)$, $c = 12.922(12)$ Å, $\beta = 114.80(5)°$ and $Z = 4$. Based on 6777 reflections the structure has been refined to $R = 0.030$ and $R_w = 0.038$. The complex is six-coordinated with *cis*-chlorides, *cis*-azo and *trans*-pyridyl groups. The overall symmetry is close to C_2. The azo N–N distances are elongated to 1.282 and 1.314 Å, significantly longer than observed in free azo groups.

The magnetic moment of 2.8 BM is independent of temperature indicating an orbitally non-degenerate low-spin ground state. In acetonitrile the spectrum shows a band in the red at 1470 nm which is assigned as ligand—metal charge transfer, consistent with earlier interpretations on similar compounds. The compound is stable to air oxidation in acetonitrile or methylene chloride; cyclic voltammetry in these solvents yields potentials of 0.508 and −0.185 V, both appearing to be one electron transfers.

The complex is a non-electrolyte in acetonitrile, nearly unchanged over 24 h. However, chloride ions are slowly replaced at 50 °C in this solvent by 2,2'-bipyridyl; this reaction is pseudo-first order in complex with a rate constant of $4.0 \pm 0.3 \times 10^{-7}$ s^{-1}. All data indicate the presence of a strong chromium—Azpy pi-interaction.

Introduction

Many studies in recent years have utilized complexes containing ligands which, in addition to being good sigma-bonding donors, also interact with the central metal in a pi-bonding fashion. The tremendous body of work on the ruthenium(II) polypyridyls is an example of this current focus. We have been interested in complexes of chelating ligands which demonstrate such interactions. One ligand of interest to us, which is just beginning to be well investigated, is 2-phenylazopyridine (Azpy).
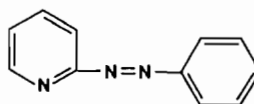
We [2, 3] and others [4–8] have demonstrated the existence of a strong pi-interaction in the ruthenium(II) complexes of this ligand. One important characteristic of Azpy is that it stabilizes reduced forms of the complexes; in Ru(Azpy)$_3$$^{2+}$ reduction led to ligand radical-anion formation [3]. With other metal ions lower oxidation states are produced; Datta and Chakravorty demonstrated the stabilization of copper(I) with this ligand, attributing the stabilization to strong metal—ligand pi-bonding [9]. Recently we have succeeded in isolating a stable rhodium(I) complex containing Azpy [10] further demonstrating this ligand property.

During the course of this work Ackermann and coworkers [11] reported the synthesis of several low valent chromium, molybdenum and tungsten complexes of this ligand starting from carbonyl precursors. Low valent $[Cr(Azpy)_3]^0$ could be isolated. In the present paper we report chemical and physical properties, including the molecular structure, of the unusually inert chromium(II) compound, $[Cr(Azpy)_2Cl_2]$.

Experimental

Materials

All organic solvents and reagents were used as received from Aldrich Chemical. Solution measurements were performed in spectrophotometric grade

---

*Presented at the 191st National Meeting of the American Chemical Society, New York, April, 1986 [1].
**Author to whom correspondence should be addressed.

solvents ('Photrex' from Baker Chemical). Azpy was synthesized as described earlier [2]. Thin-layer chromatography (TLC) utilized commercial aluminum backed silica plates (E.M. Reagents).

Preparation of Dichlorobis(2-phenylazopyridine)-chromium(II), [Cr(Azpy)$_2$Cl$_2$]

A mixture of CrCl$_3$·6H$_2$O (1.60 g) and Azpy (2.45 g) in 25 ml absolute ethanol was refluxed overnight. After standing one day a mass of dark, nearly black, crystals was isolated by filtration and washed with diethylether. Yields varied from 20 to 45%. The solid was recrystallized by dissolving in acetone, filtering, and adding an equal volume of water. After standing one day the crystals were isolated by filtration, washed with 1:1 acetone–water followed by diethylether, and dried *in vacuo* over phosphoric anhydride (90% recovery on recrystallization). TLC on the product (ethylacetate developer) showed only one component (R_f *ca.* 0.5). These crystals were suitable for crystallography. *Anal.* (Baron Consulting, Orange, Conn. 06477): Found: C, 53.85; H, 3.86; N, 17.02; Cl, 14.74. Calc. for [CrC$_{22}$H$_{18}$N$_6$Cl$_2$]: C, 54.00; H, 3.71; N, 17.18; Cl, 14.49%.

Physical Measurements

Infrared spectra were obtained on a Perkin-Elmer 283, using both mineral oil and halocarbon mulls supported on CsI plates. UV–Vis spectra were recorded using a Cary 17-D with matched silica cells.

Cyclic voltammetry data were obtained (nitrogen atmosphere) with a BAS CV-27 cyclic voltammograph using the three electrode configuration. Platinum electrodes were used and a platinum micro electrode served as a quasi-reference [12]. Data were obtained in acetonitrile containing 0.1 M NaClO$_4$; ferrocene was then run under identical conditions [13] and the data corrected to NHE assuming the ferrocene potential to be 0.400 V [14]. Spectroelectrochemical data were obtained by constructing a cell with one window being gold on quartz; this served as the working electrode. Platinum counter and reference electrodes were again used under the same conditions as for running cyclic voltammetry.

Magnetic susceptibility data were kindly provided by Dr Erik Pedersen of the Inorganic Chemistry Laboratory, H. C. Orsted Institute, Copenhagen, Denmark. The Faraday method was used over the temperature range 5 to 290 K. TIP was assumed to be 0, and appropriate diamagnetic corrections applied.

Solution conductivity measurements were made on acetonitrile solutions using an Industrial Instruments conductivity bridge, model RC 16B2. The cell had bright platinum electrodes, cell constant 0.274. Substitution kinetics were followed at 50.0 °C by observing the change in solution resistance with time.

Crystallographic Study

Suitable crystals of [Cr(Azpy)$_2$Cl$_2$] for the X-ray crystallographic study were obtained as described above. The dark irregularly shaped crystals were assigned to the monoclinic system from Weissenberg and precession photographs. Systematically absent reflections $h0l$ for l odd and $0k0$ for k odd are only consistent with the space group $P2_1/c$. Diffraction data were recorded with a CAD4 diffractometer using Mo Kα radiation obtained from a highly mosaic graphite crystal. During data collection the crystal was cooled to 105 K by an Enraf Nonius gas-flow low-temperature device; variations of the temperature measured with a thermocouple were within 1 K. Cell parameters at 105 K were determined by a least-squares refinement of the setting angles for 18 reflections, wich had θ values in the range 17–22°. Based on the profile analysis for a number of reflections the scan type and scan interval were chosen. Crystal data and some details for the data collection and structure refinement are given in Table I. Intensities of 3 standard reflections measured every 10 000 s showed that no degradation or missetting of the crystal had occurred during data collection. The maximum fluctuation was 2% from the mean.

Data were corrected for background, Lorentz and polarization effects. The symmetry related reflections were averaged, yielding 8802 independent reflections of which 6777 had $I/\sigma(I) > 2.0$. These reflections

TABLE I. Crystallographic Data for *cis*-[Cr(Azpy)$_2$Cl$_2$]

Formula	CrC$_{22}$H$_{18}$N$_6$Cl$_2$
Formula weight	489.33
Space group	$P2_1/c$
Cell parameters (105 K)	
a (A)	7.953(3)
b (A)	23.189(11)
c (A)	12.922(12)
β (°)	114.80(5)
Z	4
ρ(calc.) (g cm^{-3})	1.502
μ(Mo Kα) (cm^{-1})	7.86
Data collection	
Crystal dimensions	0.15 × 0.20 × 0.40 mm
Scan type	ω
Scan width w (°)	1.0 + 0.35 tan θ
Background	25% of full scan on both sides
Max scan time (s)	120
θ limits (°)	1–34
Octants collected	$hk \pm l\,(1-34°)\,h - k \pm l\,(1-15°)$
No. unique data	8802
Internal R values	$R = 0.018$
from averaging	$R_w = 0.020$
No. data with $I/\sigma(I)$ 2.0	6777
No. variables	352
R	0.030
R_w	0.038

TABLE II. Positional Parameters and Equivalent Isotropic Thermal Parameters

Atom	x	y	z	U_{iso}[a] (Å^2)
Cr	0.31988(3)	0.18486(1)	0.38765(2)	0.00877
Cl1	0.22577(4)	0.26835(1)	0.44808(3)	0.0139
Cl2	0.48660(4)	0.23670(1)	0.30873(3)	0.0146
N110	0.55441(14)	0.17459(4)	0.53493(9)	0.0099
C111	0.6259(2)	0.21090(5)	0.62345(10)	0.0117
C112	0.7899(2)	0.19935(6)	0.71753(11)	0.0143
C113	0.8850(2)	0.14856(6)	0.72074(11)	0.0171
C114	0.8135(2)	0.11083(6)	0.62944(12)	0.0173
C115	0.6480(2)	0.12506(5)	0.53851(11)	0.0127
N1	0.5765(2)	0.08877(5)	0.44352(9)	0.0149
N120	0.43550(14)	0.11125(5)	0.36221(9)	0.0117
C121	0.3631(2)	0.07649(6)	0.26079(11)	0.0138
C122	0.3282(2)	0.10317(7)	0.15746(12)	0.0175
C123	0.2629(2)	0.07003(7)	0.05855(13)	0.0224
C124	0.2303(2)	0.01160(7)	0.06348(14)	0.0246
C125	0.2624(2)	−0.01421(7)	0.16671(14)	0.0239
C126	0.3309(2)	0.01784(6)	0.26680(13)	0.0186
N210	0.0843(2)	0.17752(5)	0.24247(9)	0.0114
C211	0.0381(2)	0.20494(6)	0.14200(11)	0.0150
C212	−0.1261(2)	0.19448(7)	0.04825(11)	0.0193
C213	−0.2496(2)	0.15406(7)	0.05689(12)	0.0231
C214	−0.2052(2)	0.12543(7)	0.15820(12)	0.0221
C215	−0.0367(2)	0.13823(6)	0.25061(11)	0.0141
N2	0.0079(2)	0.11160(5)	0.35380(9)	0.0148
N220	0.16361(14)	0.13208(4)	0.43174(9)	0.0107
C221	0.2115(2)	0.10600(5)	0.54071(10)	0.0110
C222	0.1892(2)	0.04668(6)	0.54962(11)	0.0141
C223	0.2296(2)	0.02258(6)	0.65558(12)	0.0164
C224	0.2930(2)	0.05724(6)	0.75247(11)	0.0164
C225	0.3178(2)	0.11623(6)	0.74351(11)	0.0148
C226	0.2780(2)	0.14076(6)	0.63752(11)	0.0126

[a] $U_{iso} = \frac{1}{3} \Sigma_{ij} U_{ij} \bar{a}_i \bar{a}_j a_i^* a_j^*$ for atoms refined with anisotropic thermal parameters.

were classified as observed and used in the subsequent structure determination and refinement. The $\sigma(I)$ values were calculated using counting statistics.

Structure Determination and Refinement

The structure was solved by the heavy atom method using Patterson and Fourier methods. The calculations were performed with the SDP-system [15] using a data set with $\theta_{max} = 20°$, while the data collection was completed. Positions for all non-hydrogen atoms were localized and refined with isotropic temperature factors with this data set.

The X-ray System [16] was used for the final crystallographic computations with the full data set. The structure was refined by the method of least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken from Cromer and Wabers tabulation [17], using the values for the uncharged atoms, except for hydrogen for which the values of Stewart *et al.* [18] were employed. Atomic scattering factors for Cr and Cl were corrected for the effects

of anomalous dispersion by using the values given by Cromer and Liberman [19].

After anisotropic thermal parameters were introduced and refined for all the non-hydrogen atoms a difference Fourier clearly showed the positions for all the hydrogen atoms. Positional and isotropic thermal parameters for the hydrogen atoms were also included in the final cycles of least-squares refinement, where the weights were changed from unit weights to weights following the expression $w^{-1} = 3\sigma^2(F) + 0.0005|F|^2$. The coefficients were chosen to make $\langle w \Delta F^2 \rangle$ evenly distributed in F_o. The refinement of the 352 parameters converged at the R values $R = 0.030$ and $R_w = 0.038$, the maximum shift in the last cycle was 0.05σ. A final difference Fourier map had maximum peaks of 0.6 $\text{e}/\text{Å}^3$, which could be interpreted as residual bonding density in the phenyl groups. An analysis of $|F_o|$ and $|F_c|$ values showed that the data do not suffer from the effects of secondary extinction. Final positional parameters of the individual non-hydrogen atoms are given in Table II. See also 'Supplementary Material'.

TABLE III. Bond Lengths (Å) and Bond Angles (°)

Cr–N110	2.044(2)	Cr–N210	2.027(2)
Cr–N120	2.0300(14)	Cr–N220	1.9903(14)
Cr–Cl1	2.3258(10)	Cr–Cl2	2.3189(11)
N110–C111	1.340(2)	N210–C211	1.351(2)
C111–C112	1.386(2)	C211–C212	1.380(2)
C112–C113	1.391(2)	C212–C213	1.395(3)
C113–C114	1.385(2)	C213–C214	1.376(3)
C114–C115	1.387(2)	C214–C215	1.403(2)
C115–N110	1.359(2)	C215–N210	1.361(2)
C115–N1	1.397(2)	C215–N2	1.374(2)
N1–N120	1.282(2)	N2–N220	1.314(2)
N120–C121	1.437(2)	N220–C221	1.430(2)
C121–C122	1.390(2)	C221–C222	1.398(2)
C122–C123	1.392(2)	C222–C223	1.386(2)
C123–C124	1.386(3)	C223–C224	1.392(2)
C124–C125	1.385(3)	C224–C225	1.394(2)
C125–C126	1.390(2)	C225–C226	1.391(2)
C126–C121	1.392(6)	C226–C221	1.393(2)
Cl1–Cr–Cl2	92.29(3)	N120–Cr–N220	84.77(6)
Cl1–Cr–N10	94.64(8)	Cl2–Cr–N210	96.51(6)
Cl1–Cr–N120	170.34(8)	Cl2–Cr–N220	170.26(7)
Cl1–Cr–N210	94.47(5)	Cl2–Cr–N110	90.18(6)
Cl1–Cr–N220	95.07(4)	Cl2–Cr–N120	89.05(4)
N110–Cr–N120	75.79(5)	N210–Cr–N220	76.57(5)
N110–Cr–N210	168.46(9)	N120–Cr–N220	84.77(6)
N110–Cr–N220	95.88(5)	N210–Cr–N120	94.88(5)
Cr–N110–C111	128.05(9)	Cr–N210–C211	128.56(10)
Cr–N110–C115	113.76(8)	Cr–N210–C215	113.18(9)
Cr–N120–N1	120.59(9)	Cr–N220–N2	120.24(10)
Cr–N120–C121	125.71(8)	Cr–N220–C221	126.99(8)
C115–N110–C111	118.16(10)	C215–N210–C211	118.24(10)
N110–C111–C112	122.26(13)	N210–C211–C212	122.47(15)
C111–C112–C113	119.32(12)	C211–C212–C213	119.10(14)
C112–C113–C114	119.05(11)	C212–C213–C214	119.50(12)
C113–C114–C115	118.44(14)	C213–C214–C215	118.7(2)
C114–C115–N110	122.77(11)	C214–C215–N210	122.01(13)
C114–C115–N1	119.52(13)	C214–C215–N2	119.78(15)
N110–C115–N1	117.65(9)	N210–C215–N2	118.19(10)
C115–N1–N120	111.63(12)	C215–N2–N220	111.00(13)
N1–N120–C121	113.42(12)	N2–N220–C221	112.22(12)
N120–C121–C122	117.95(13)	N220–C221–C222	120.45(10)
N120–C121–C126	120.64(13)	N220–C221–C226	118.94(12)
C121–C122–C123	118.93(15)	C221–C222–C223	119.55(12)
C122–C123–C124	120.17(15)	C222–C223–C224	120.15(14)
C123–C124–C125	120.29(15)	C223–C224–C225	120.15(14)
C124–C125–C126	120.5(2)	C224–C225–C226	120.08(12)
C125–C126–C121	118.69(15)	C225–C226–C221	119.45(13)
C126–C121–C122	121.41(13)	C226–C221–C222	120.60(12)

Results and Discussion

Synthesis and Chemical Characterization

The complex $[Cr(Azpy)_2Cl_2]$ is readily prepared by heating hydrated chromium(III) chloride and the ligand in ethanol, with the product slowly crystallizing. Yields are variable but rarely exceed 30%. Since the compound is insoluble in the reaction medium and the filtrate is highly colored we conclude this compound to be only one of several being formed. Once we had established that the product was a chromium(II) compound we attempted a synthesis starting with chromous chloride generated in ethanol; no improvement in yield resulted.

In contrast to our earlier work with ruthenium where three isomers were isolated [2], only one

isomer of $[Cr(Azpy)_2Cl_2]$ has been detected. This is surprising in view of the inert nature of this compound (below); it may well be that other isomers show considerably greater reactivity and are partially responsible for the low yields obtained; TLC of the reaction mixture shows no evidence for other uncharged compounds.

We have not obtained other complexes from this compound although substitution reactions of the chloro-groups do occur. Mixing $[Cr(Azpy)_2Cl_2]$ with hydrobromic acid results in a new compound, presumably $[Cr(Azpy)_2Br_2]$, which is similar to the starting material. This product consistently gives poor analyses and has not been characterized.

$[Cr(Azpy)_2Cl_2]$ is a non-electrolyte in acetonitrile. On standing in this solvent there is a slow increase in conductivity (*ca.* 1% in 24 h) indicating some chloride displacement. However, addition of 2,2'-bipyridyl (bpy) leads to chloride substitution. Assuming the final product to be $[Cr(Azpy)_2bpy]^{2+}$, and using an average value of the molar conductivity of a 2:1 electrolyte in this solvent of 300 ohm^{-1} cm^2 mol^{-1} [20] we have determined the pseudo-first order rate constant (with ten-fold excess of bpy) for this reaction to be $4.0 \pm 0.3 \times 10^{-7}$ s^{-1}. Different values for the molar conductivity change this constant but not its order of magnitude. The compound is unquestionably inert to substitution.

The inert nature of $[Cr(Azpy)_2Cl_2]$ stands in contrast to that 'normally' observed for chromium-(II). A similar situation appears to occur in chromium-(II) arylisonitrile complexes [21] although slow solution decomposition occurs in this case [22] indicating lower stability than we observe here. We conclude that Azpy has rather unique ligand properties, much more like those observed for isonitriles than for the bipyridyl type ligands. To our knowledge, the above rate constant is the first to be reported for a low-spin chromium(II) compound.

Description of the Structure

The molecular geometry of the compound is illustrated by the ORTEP drawing in Fig. 1 and by the bond lengths and angles in Table III. The drawing illustrates that the molecule almost possesses a non-crystallographic two-fold axis of symmetry. The conformations of the two Azpy ligands differ only slightly (6°) as shown by the torsion angles listed in Table IV. This is in contrast to the stereochemistry observed in the *cis*-azido complex, $[Ru(Azpy)_2(N_3)_2]$ [23]. Here, the crystal structure is formed by two conformers of the complex, one of which has an overall symmetry which is close to C_2 but the geometry of the other conformer is completely irregular. Although Taylor and Kennard [24] have recently shown that the standard deviations obtained from a crystal structure refinement appear to be underestimated by a factor of 2 there seem to be
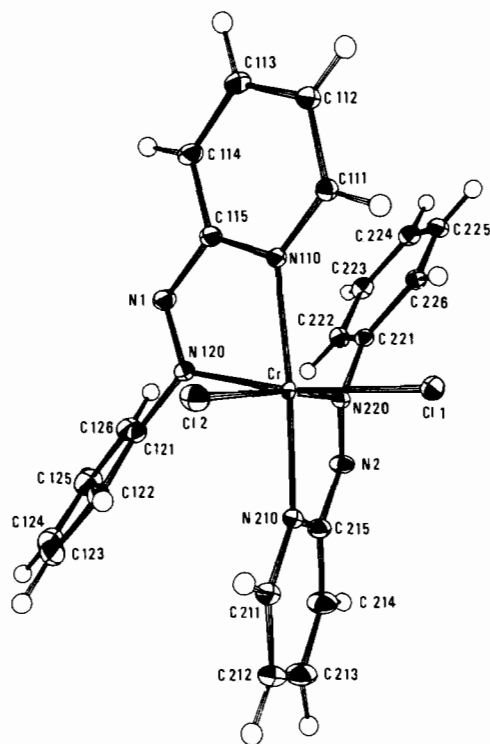

Fig. 1. Perspective view of *cis*-$[Cr(Azpy)_2Cl_2]$. The thermal ellipsoids are scaled to include 50% probability. The hydrogen atoms are drawn as spheres with an arbitrary radius.

TABLE IV. Torsion Angles (°)

C114–C115–N1–N120	−172.42(14)
N110–C115–N1–N120	4.7(2)
C115–N1–N120–C121	177.17(2)
N1–N120–C121–C122	−131.35(15)
N1–N120–C121–C126	48.1(2)
C214–C215–N2–N220	−175.34(15)
N210–C215–N2–N220	3.3(2)
N2–N220–C221–C222	41.7(2)
N2–N220–C221–C226	−137.27(13)

significant variations in the molecular geometry of $[Cr(Azpy)_2Cl_2]$. While the molecular symmetry is close to C_2 a closer inspection of Table III reveals some differences between the two symmetry related parts of the molecule. This is pronounced both in the coordination sphere around chromium as well as in the molecular distances within the ligand. The Cr–N220 distance of 1.990 Å is significantly shorter than the Cr–N120 distance of 2.030 Å. The N1–N120 and N2–N220 distances are also significantly different being 1.282 and 1.314 Å respectively. Except for the part of the ligand which is affected by this change the other dimensions are more similar in the two ligands and comparable with the geometry of the Azpy ligand found in $[Ru(Azpy)_2(N_3)_2]$ [23].
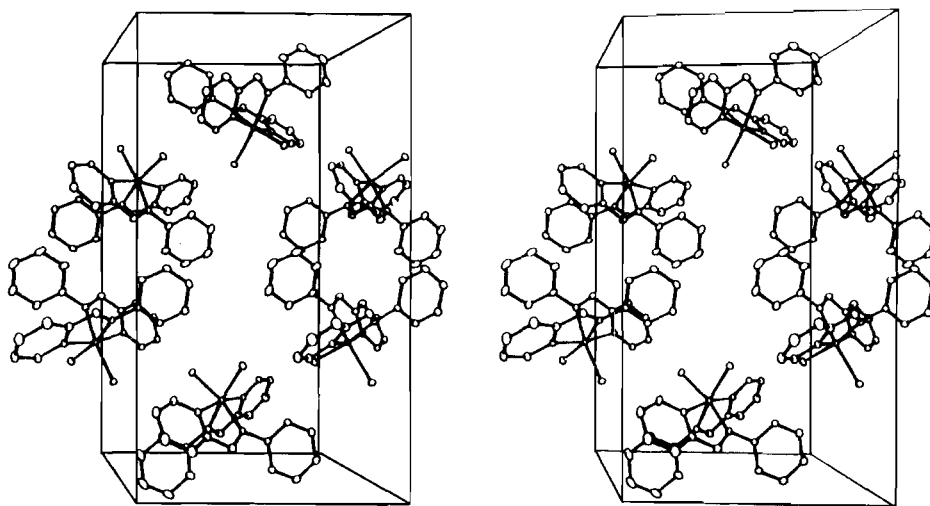
Fig. 2. Stereo pair illustrating the packing in *cis*-[Cr(Azpy)$_2$Cl$_2$] viewed along a^*.

To illustrate the stereochemistry least-squares planes have been calculated for the pyridine and phenyl groups. These six-membered rings are all planar, the angle between the two pyridine rings is 74°, which is very similar to the angles of 68° and 71° found in [Ru(Azpy)$_2$(N$_3$)$_2$]. The phenyl groups are almost parallel, the angle between the two least-squares planes being 2°. Packing in the crystal, illustrated by the stereo pair in Fig. 2, is determined by van der Waals interactions. No intermolecular distances are shorter than the sum of the van der Waals radii.

Chromium(II)—nitrogen bond distances in [Cr(Azpy)$_2$Cl$_2$] are shorter than those previously observed in complexes containing pyridine ligands. Examples are the high-spin nicotinate complex [Cr(H$_2$O)$_4$(nic)$_2$] (Cr—N = 2.128 Å) [25] and the low-spin tetraphenylporphyrinbispyridine compound, [Cr(TPP)(py)$_2$] (Cr—N(py) = 2.121 and 2.141 Å) [26]. Cr—N bond distances to the porphyrin nitrogens in this latter compound (2.012 to 2.044 Å) [26] are much closer to those found in the present study.

A better complex for comparison, perhaps, is the chromium(III) complex, [Cr(bpy)$_2$(H$_2$O)Cl]$^{2+}$ where Cr—N distances are 2.037 and 2.059 Å [27]. Since shorter metal—ligand distances are anticipated in chromium(III) than in chromium(II) compounds there is the implication of strong bonding interactions in [Cr(Azpy)$_2$Cl$_2$]. Takemoto *et al.* [28] argued that stronger pi-interactions as chromium is reduced in the series of complexes [Cr(bpy)$_3$]$^{n+}$ was the rational for little change in M—L vibrational energies. We have already pointed out the tendency for azo ligands to participate in pronounced M—L pi-bonding in the case of ruthenium(II) complexes [2, 3, 23, 29] and feel that all data support a similar interaction in [Cr(Azpy)$_2$Cl$_2$].

TABLE V. Comparison of Azo Bond Distances

	N N (Å)	Reference
[Cr(Azpy)$_2$Cl$_2$]	1.282, 1.314	this work
[Ru(Azpy)$_2$Cl$_2$](C$_2$)	1.279, 1.283	32
(C$_1$)	1.30, 1.29	
[Ru(Azpy)$_2$(N$_3$)$_2$]	1.288, 1.289	23
	1.299, 1.291	
trans C$_6$H$_5$N NC$_6$H$_5$	1.24	47

Bohling and Mann [30], in comparing a series of isonitrile complexes containing chromium in varying oxidation states, noted an increase in Cr—C bond lengths with increasing metal charge, *i.e.* the reverse of the usual trend. They commented that this was consistent with decreasing M—L pi-interaction; we conclude this to be important in the present study.

Further support for this view comes from a comparison of the azo-N—N bond distances in several compounds (Table V). It can be seen that the azo-distance in the three complexes compared here are all longer than that in azobenzene, which should contain a representative 'normal' azo-distance. Also, the shorter Cr—N(azo) bond is to the ligand having the longer N—N distance. The implication is that [Cr(Azpy)$_2$Cl$_2$] contains a pronounced Cr—Azpy pi-interaction, and further that this interaction is not the same for the two Azpy ligands. Infrared results (below) are consistent with this view.

Cr—Cl distances are as anticipated. While this distance in [Cr(bpy)$_2$(H$_2$O)Cl]$^{2+}$ is 2.259 Å our compound shows 2.3258 and 2.3189 Å, significantly longer than in chromium(III) as anticipated. We are aware of structural data for only one other low-spin

TABLE VI. Infrared Bands in the Metal–Ligand Region (cm^{-1})[a]

$[Cr(Azpy)_2Cl_2]$	$[Ru(Azpy)_2Cl_2]$	$[Cr(bpy)_3]^{2+}$	Assignment
412s	440s		
375m	376s		M–N(azo)
364s	358m	351s	M–N(py)
330s	336s		M–Cl
303sh	308s		
285sh	304sh		M–Cl
276w	280m		M–N(azo)
262m	268s	343s	M–N(py)
247w			

[a]azo = azo-nitrogen; py = pyridine nitrogen; s = strong; m = medium; w = weak; sh = shoulder; all spectra measured on mineral oil mulls of the solids.

TABLE VII. Reduction Potentials in Acetonitrile (V)

	III/II	II/I	Reference
$[Cr(Azpy)_2Cl_2]$	0.508(64)[a, b]	−0.185(82)	this work
$[Cr(Azpy)_3]^{n+}$	1.06[c]	0.50	11
$[Cr(bpy)_3]^{n+}$	−0.26[c]	−0.76	35
$[Cr(CNC_6H_5)_6]^{n+}$	0.66[d]	−0.09	37

[a]Difference between cathodic and anodic sweeps (mV).   [b]Corrected to NHE by reference to ferrocene.   [c]Reported *vs.* SCE.   [d]Reported *vs.* Ag/AgCl, corrected to ferrocene.

chromium(II) compound containing coordinated chlorides [31]. In this compound (containing a chelating alkyl phosphine) Cr–Cl distances of 2.333 and 2.328 Å were found, essentially the same as we observe. We conclude that there are no unusual bonding features present in the Cr–Cl bonds of $[Cr(Azpy)_2Cl_2]$.

Infrared Spectrum

$[Cr(Azpy)_2Cl_2]$ and α-$[Ru(Azpy)_2Cl_2$ [2] have similar geometric structures [2, 32]. In Table VI infrared bands in the M–L region of the two compounds are summarized and assignments made. Takemoto *et al.* [28] have assigned Cr–N vibrational modes in $[Cr(bpy)_3]^{2+}$ and these are included for comparison.

The similarity between band positions for [Cr-(Azpy)$_2$Cl$_2$] and $[Ru(Azpy)_2Cl_2]$ in this region is striking. Stronger bonding in the ruthenium(II) compound is offset by the greater reduced mass, resulting in little difference between the two. Takemoto *et al.* [28] demonstrated a similar opposition of bonding parameters in their comparison of the $[Cr(bpy)_3]^{n+}$ complexes, where band energies varied little with changing charge on the central chromium, due to decreasing pi-interaction with increasing metal charge.

A notable difference in the spectra of the chromium(II) and ruthenium(II) complexes occurs in the

1100 cm^{-1} region. While the azo-stretching mode appears at 1323 and 1295 cm^{-1} in $[Ru(Azpy)_2Cl_2]$ the chromium(II) compound shows two strong bands centered at 1123 and 1085 cm^{-1}. These values should be compared with that of the free ligand at 1424 cm^{-1} [2]. (Ackermann *et al.* [11] found the azo-stretching mode in $[Cr(CO)_4Azpy]$ at 1288 cm^{-1}). This difference is consistent with the long N–N bonds (compared to normal azo-distances) found in the crystal structure. Earlier we related the azo-infrared vibration to extent of pi-interaction [2, 3] between metal and ligand. Whether the pi-bonding is ligand to metal or metal to ligand the azo bond order should decrease; in the present case we feel the data support a strong interaction but the exact nature of this is difficult to assign.

Electrochemistry

Cyclic voltammetry results are recorded in Table VII along with results of several other workers for chromium complexes. While chromium(III) is generally the most stable oxidation state (e.g. reduction of $Cr(H_2O)_6^{3+}$ has $E^0 = -0.41$ V [33]) there are exceptions, particularly among low-spin chromium(II) complexes containing pi-interacting ligands. Thus, stabilization of chromium(II) in $[Cr(Azpy)_2Cl_2]$ is

not without precedent, and the 0.5 V potential (for the III/II reduction) explains the solution stability of the complex.

A second reduction appears at a potential of −0.185 V. This is for the formal II/I process although it might very well correspond to ligand radical-anion formation, as observed earlier in $[Ru(Azpy)_3]^{2+}$ [3].

Ackermann et al. [11] have observed a potential of 1.06 V (versus SCE) for the $[Cr(Azpy)_3]^{n+}$ (III/II) couple which is consistent with our observation in $[Cr(Azpy)_2Cl_2]$. These results should be compared to those for $[Cr(bpy)_3]^{n+}$. Brunschwig and Sutin found the III/II potential to be −0.26 V (versus NHE) in aqueous solution [34]. Saji and Aoyagui obtained the same value in acetonitrile referenced against the SCE [35], while Hughes and Macero [36] observed the (III/II) potential at −0.209 V (versus Ag/AgCl in acetonitrile). The latter two groups found the (II/I) potential near −0.7 V. In the absence of a standard (e.g. ferrocene) junction potential uncertainties make conversion to a common scale difficult. However, a reasonable estimate for the (II/I) potential in $[Cr(bpy)_3]^{n+}$ versus NHE is −0.5 V. This is the value we have assumed in the discussion of the optical 'red' band (below).

Bohling et al. [37] found the potential for Cr(III/II) in the phenylisonitrile complex to indicate a stabilization of chromium(II), as we find in $[Cr(Azpy)_2Cl_2]$. Like our compound, $[Cr(CNC_6H_5)_6]^{2+}$ contains low-spin chromium(II) [22]. The ligator properties of Azpy appear to be quite different from those of conventional nitrogen donors, but instead more similar to isonitriles or phosphines. Ackermann et al. [11] have concluded Azpy to be a weak sigma-donor and strong pi-acceptor, consistent with our observations.

Magnetic Measurements

Magnetic susceptibility data as a function of temperature have been obtained for $[Cr(Azpy)_2Cl_2]$. The calculated magnetic moment values are graphed in Fig. 3. Two important features become apparent: the effective magnetic moment is near 2.8 BM, and the moment is essentially independent of temperature above 20 K. The complex thus contains low-spin chromium(II), and the ground state is of low orbital degeneracy.

Several six-coordinate chromium(II) compounds have been observed to be low spin; these are all complexes with strong-field ligands. In no cases have interpretations of the data been obvious. Earnshaw et al. [38] found the temperature dependence of moment for $[Cr(bpy)_3]Br_2$ to deviate from that predicted by the Kotani model [39]. It was suggested that differences could arise from metal electrons delocalizing onto the ligands and the presence of low-symmetry components. Terezakis and Carlin [40] fit these data to the theory developed by Figgis and co-
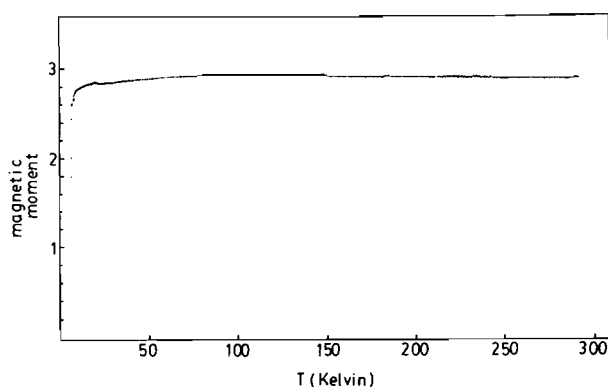

Fig. 3. Magnetic moment (BM) vs. temperature for cis-$[Cr(Azpy)_2Cl_2]$.

workers [41] for $^3T_1$ states undergoing distortion. But Lutz et al. [42] suggested this theory was not applicable to the problem because of deviation from cubic symmetry. These authors were able to obtain data to much lower temperatures than the early reports allowing a better analysis.

Desai et al. [43] have studied the magnetic properties of chromocene over an extended temperature range and have successfully fit the data to a model including a dynamic Jahn—Teller effect. They found that large reductions in spin—orbit coupling and in the orbital reduction factor, assumed necessary in other compounds, were not required.

In view of the low symmetry shown by $[Cr(Azpy)_2Cl_2]$ it is reasonable to expect the $^3T_{1g}$ ground term of a cubic system to be split into orbitally non-degenerate states. We must conclude that this splitting is large enough that mixing-in of higher states does not influence the magnetic moment, and the behavior is essentially that observed in chromocene.

Optical Spectrum

The optical solution spectrum of $[Cr(Azpy)_2Cl_2]$ shows features observed in earlier studies on other low-spin chromium(II) complexes (Table VIII). $[Cr(bpy)_3]^{2+}$ [44], $[Cr(bpy)_2(NCS)_2]$ [45] and $[Cr(pdma)_2Cl_2]$ (pdma = o-bis(dimethylarsine)benzene) [46] all show strong bands in the red near 1200 nm; in $[Cr(Azpy)_2Cl_2]$ a similar band appears at 1470 nm. In the LF region the bpy complexes show several medium intensity red bands. König and Herzog assigned these as LF mixed with charge-transfer [44]; they were able, however, to account for the energies of these bands using simple ligand field theory.

Applying König and Herzog's treatment of 'LF' bands in $[Cr(Azpy)_2Cl_2]$ we account for the observed transitions in the visible spectrum using 10 Dq of ca. 16 500 and 800 cm^{-1} for B. The B value, which is close to that of the free ion, is reasonable in that the magnetic data do not require a large orbital reduction

TABLE VIII. Optical Absorption Spectra

	Solvent	Energy (cm^{-1}) (molar absorption coefficient)			Reference
$[Cr(Azpy)_2Cl_2]$	a	6800(4400) 14900(960) 29000(17600)	13200(1120) 15100(sh)		this work
$[Cr(bpy)_2(NCS)_2]$	b	8400(vs) 19600(s)	13400(s)	16400(s)	45
$[Cr(bpy)_3]^{2+}$	c	8700(10000) 14500(2300)	9900(2900) 17800(4850)	12050(1700) 21600(4150)	44
$[Cr(pdma)_2Cl_2]^d$	b	7400 8800	15400(sh)	>20000	46

[a] Acetonitrile.   [b] Solid, (s = strong; v = very; sh = shoulder).   [c] Methanol.   [d] pdma = 1,2-bis(dimethylarsine)benzene.

factor. Desai *et al.* in explaining the chromocene magnetics [43] found this to be unnecessary; the similarity between our data and their observations lends credence to this argument.

This spectral analysis assumes cubic microsymmetry. In view of the known low symmetry of [Cr-(Azpy)$_2$Cl$_2$] it is questionable how correct such a treatment can be; the major point is that the calculated transitions within the O_h model lie within the observed band envelopes.

König and Herzog assigned the far red bands (observed in $[Cr(bpy)_3]^{2+}$ at 8700 and 9900 cm^{-1}) as ligand to metal CT. In order to gain further information on this transition in $[Cr(Azpy)_2Cl_2]$ we examined the complex spectroelectrochemically in acetonitrile. As the compound was oxidized in the cell both the 1470 nm and chromium(II) LF bands diminished in intensity, while a new strong band developed below 500 nm. On reduction the original spectral features redeveloped. Steady diminution of the 1470 nm band during oxidation seems to eliminate the possibility of this band being intervalence, due to the presence of oligomeric solution species.

To explain the origin of the far red band we note that the transition occurs at lower energy for [Cr-(Azpy)$_2$Cl$_2$] than for $[Cr(bpy)_3]^{2+}$. Assuming a common transition in both complexes L—M is the favored explanation. Reduction of $[Cr(Azpy)_2Cl_2]$ occurs at a more positive potential than for $[Cr(bpy)_3]^{2+}$; thus, a lower energy transition is anticipated in the former. If the transition were M—L we would expect the band in $[Cr(Azpy)_2Cl_2]$ to appear at higher energy than in the bpy complex since the oxidation potential is far less favorable in the former.

Supplementary Material

Tables of 'Anisotropic thermal parameters for non-hydrogen atoms', 'Coordinates and isotropic thermal

parameters for the hydrogen atoms', and 'Lists of observed and calculated structure amplitudes' are available from the authors on request.

References

1 V. Ferreira, R. A. Krause and S. Larsen, *191st National Meeting of the American Chemical Society*, New York, N.Y., April 1986, Abstr. INOR 368.
2 R. A. Krause and K. Krause, *Inorg. Chem.*, *19*, 2600 (1980).
3 R. A. Krause and K. Krause, *Inorg. Chem.*, *21*, 1714 (1982).
4 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, *20*, 2246 (1981).
5 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, *21*, 2737 (1982).
6 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, *22*, 602 (1983).
7 S. Goswami, R. Mukherjee and A. Chakravorty, *Inorg. Chem.*, *22*, 2825 (1983).
8 D. Datta, *J. Chem. Soc., Dalton Trans.*, 1907 (1986).
9 D. Datta and A. Chakravorty, *Inorg. Chem.*, *22*, 1085 (1983).
10 J. J. Robertson, *M.S. Thesis*, University of Connecticut, 1986.
11 M. N. Ackermann, C. R. Barton, E. M. Specht and W. E. Schreiber, '187th National Meeting of the American Chemical Society, St. Louis, Mo, U.S.A.', American Chemical Society, Washington, D.C., 1984, Abstr. INOR 133.
12 D. J. Fisher, W. L. Belew and M. T. Kelley, *ORNL-P-14, Chem. Abstr.*, *62*, 7081 (1965).
13 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, *19*, 2854 (1980).

14 H. M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem., 64*, 483 (1960).

15 B. A. Frenz, 'Enraf-Nonius Structure Determination Package', SPD-PLUS version 1.1, 1983.

16 'X-ray System', *Technical Report TR-446*, Computer Science Center, University of Maryland, College Park, Md., 1976.

17 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974, Table 2.2A.

18 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42*, 3175 (1965).

19 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53*, 1891 (1970).

20 W. J. Geary, *Coord. Chem. Rev., 7*, 81 (1971).

21 D. A. Bohling and K. R. Mann, *Inorg. Chem., 22*, 1561 (1983).

22 P. M. Treichel and G. J. Essenmacher, *Inorg. Chem., 15*, 146 (1976).

23 K. Krause, R. A. Krause, S. Larsen and B. Rasmussen, *Acta Chem. Scand. Ser. A, 39*, 375 (1985).

24 R. Taylor and O. Kennard, *Acta Crystallogr., Sect. B, 42*, 112 (1986).

25 W. E. Broderick, M. R. Pressprich, U. Geiser, R. D. Willett and J. I. Legg, *Inorg. Chem., 25*, 3372 (1986).

26 W. R. Scheidt, A. C. Brinegar, J. F. Kirner and C. A. Reed, *Inorg. Chem., 18*, 3610 (1979).

27 W. A. Wickramasinghe, P. H. Bird, M. A. Jamieson, N. Serpone and M. Maestri, *Inorg. Chim. Acta, 64*, L85 (1982).

28 J. Takemoto, B. Hutchinson and K. Nakamoto, *J. Chem. Soc. D*, 1007 (1971).

29 R. A. Krause and K. Krause, *Inorg. Chem., 23*, 2195 (1984).

30 D. A. Bohling and K. R. Mann, *Inorg. Chem., 23*, 1426 (1984).

31 A. M. Arif, J. G. Hefner, R. A. Jones and B. R. Whittlesey, *Inorg. Chem., 25*, 1080 (1986).

32 A. Seal and S. Ray, *Acta Crystallogr., Sect. C, 40*, 929 (1984).

33 D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc., 65*, 1897 (1943).

34 B. Brunschwig and N. Sutin, *J. Am. Chem. Soc., 100*, 7568 (1978).

35 T. Saji and S. Aoyagui, *Electroanal. Chem., 60*, 1 (1975).

36 M. C. Hughes and D. J. Macero, *Inorg. Chem., 15*, 2040 (1976).

37 D. A. Bohling, J. F. Evans and K. R. Mann, *Inorg. Chem., 21*, 3546 (1982).

38 A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin and E. G. Terezakis, *J. Chem. Soc, A*, 511 (1966).

39 M. Kotani, *J. Phys. Soc. Jpn., 4*, 293 (1949).

40 E. G. Terezakis and R. L. Carlin, *Inorg. Chem., 6*, 2125 (1967).

41 B. N. Figgis, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc. A*, 1411 (1966).

42 P. M. Lutz, G. J. Long and W. A. Baker, Jr., *Inorg. Chem., 8*, 2529 (1969).

43 V. P. Desai, E. König and B. Kanellakopulos, *J. Chem. Phys., 78*, 6299 (1983).

44 E. König and S. Herzog, *J. Inorg. Nucl. Chem., 32*, 585 (1970).

45 A. Earnshaw, L. F. Larkworthy, K. C. Patel and B. J. Tucker, *J. Chem. Soc., Dalton Trans.*, 2209 (1977).

46 F. Mani, P. Stoppioni and L. Sacconi, *J. Chem. Soc., Dalton Trans.*, 461 (1975).

47 C. J. Brown, *Acta Crystallogr., 21*, 146 (1966).