$$\frac{(\Delta \ln k)_E{}^{x_r}}{(\Delta \ln k)_E{}^{x_2}} = 1 + 4.3\left(\frac{x_2 - x_r}{x_2 - x_i}\right) \tag{8}$$

However, the use of eq 8 to account for the large difference shown in Table I for the kinetic response to iodide adsorption of, for example, the hexaaquo and hexaammine complexes would require that the ratio $(x_2 - x_r)/(x_2 - x_i)$ have the very large value of ca. 0.8. (If this ratio were unity, the reaction site would lie on the iHp.) For this reason we believe the iodide response data also reflect the presence of specific interactions between the adsorbed iodide anions and the cationic complexes within the inner portion of the double layer. Specific effects of this type have been frequently proposed to account for the kinetic behavior of more complex electrode reactions (especially anion reductions) for which the site of reaction is thought to lie within the compact layer.[14-19] We found no evidence of such effects in previous studies of the reduction of the cationic aquo complexes of chromium(III) and europium(III)[4,20] but that is to be expected if aquo complexes in general have reaction sites within the outer, diffuse portion of the double layer where the charges on the discrete, adsorbed anions can be screened by the high ionic conentrations within the diffuse layer.

The dipositive ammine complexes in Table I all show rate enhancements in the presence of adsorbed iodide which are larger than that of the dipositive, outer-sphere analogue $Cr(OH)_2)_5F^{2+}$. This probably results because these complexes react by both inner-sphere and outer-sphere pathways which are more competitive than was true for the pentaaquo series because the ammine complexes can approach the electrode surface more closely, even when they react by an outer-sphere pathway. The iodide adsorption test cannot provide a clear distinction between reaction mechanisms, of course, in cases where neither pathway is kinetically predominant. The successful use of this test with the pentaaquo complexes[1] depended upon the rates of inner-sphere pathways being so much larger than those of outer-sphere pathways that the iodide enhancement of the latter was more than counterbalanced by its repression of the former. The single complex in Table I which shows a decreased rate upon iodide adsorption, *trans*-$Cr(en)_2(NCS)^+$, is also very strongly adsorbed on mercury.[21] Its response to iodide adsorption seems a clear signal that this complex is reduced predominantly by an inner-sphere mechanism. The relatively large value of α_{app} for this complex could reflect a parallel and less efficient outer-sphere pathway but, more likely, it results from the increase in the adsorption of the complex with more negative potentials[21]—a trend which is opposite from that observed with most isothiocyanato complexes of Cr(III). Values of α_{app} larger than 0.5 are to be expected[1] for inner-sphere reactants which show increased adsorption at more negative potentials.

Conclusions

As suggested by Weaver[9] the data summarized in Table I can be interpreted as indicating that $Cr(NH_3)_6{}^{3+}$, $Cr(NH_3)_5OH_2{}^{3+}$, and *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ are reduced at mercury by outer-sphere mechanisms in which the reaction site lies closer to the mercury surface than it does during the outer-sphere reduction of $Cr(OH_2)_6{}^{3+}$. With the exception of $Cr(NH_3)_5F^{2+}$, the dipositive and monopositive complexes in Table I appear to be reduced by parallel inner-sphere and outer-sphere pathways at rates that are too similar to permit mechanistic diagnoses as clear-cut as proved possible with analogous pentaaquo complexes.[1] The ability of the ammine complexes to approach the electrode surface more closely than the aquo complexes appears to be the origin of the greater reactivity displayed by the former complexes in their outer-sphere reduction at electrodes. The previously proposed criteria for distinguishing between inner- and outer-sphere electrode reaction pathways[1] are not vitiated by the results presented here but it seems clear that the demands on the quantity and precision of kinetic data will be much greater if rate constants for both inner- and outer-sphere pathways are to be evaluated when they make comparable contributions to overall reaction rates.

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Registry No. $Cr(NH_3)_6{}^{3+}$, 14695-96-6; $Cr(NH_3)_5OH_2{}^{3+}$, 15975-47-0; *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, 42402-01-7; $Cr(OH_2)_6{}^{3+}$, 14873-01-9; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_3)_5NO_3{}^{2+}$, 21350-86-7; $Cr(NH_3)_5N_3{}^{2+}$, 22317-10-8; $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $Cr(NH_3)_5F^{2+}$, 19443-25-5; $Cr(H_2O)_5F^{2+}$, 19559-07-0; *trans*-$Cr(en)_2Cl_2{}^+$, 14403-88-4; *trans*-$Cr(en)_2(NCS)_2{}^+$, 29845-02-1; $Cr(OH_2)_5OSO_3{}^+$, 19163-97-4.

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Temperature and Pressure Effects on the Electronic Transitions of Nickel(II) Complexes with *C,C*-Dimethylethylenediamine and *N,N*-Dimethylethylenediamine[1]

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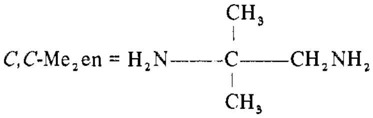
Complexes of the type $M(Et_2en)_2X_2$, where M = Cu(II) or Ni(II), Et_2en = *N,N*-diethylethylenediamine and X = an inorganic anion, manifest thermochromic behavior.[3-8] Lever and co-workers[5-6] have provided convincing support for a model of tetragonal distortion in these complexes, in which the in-plane bond strength increases as the axial ligation decreases, as the mechanism for thermochromism.[6] Pressure and thermal studies of the copper and nickel complexes in the electronic and infrared regions (mid- and far-infrared) by Ferraro et al.[8] have confirmed Lever's mechanism as the

Table I. Comparison of Temperature and Pressure Effects on the Electronic Transition of Ni(C,C-Me$_2$en)$_2$X$_2$ Thermochromic Complexes[a]

X^-	T, °C	Max abs, µm^{-1}	Δ_{abs}(LT–HT), µm^{-1}	Pressure (25 °C), kbar	Max abs, µm^{-1}	Δ_{abs}(44–0 kbar), µm^{-1}
			Ni(C,C-Me$_2$en)$_2$X$_2$			
BF_4^-	20	2.260	−0.048	0	2.273	0.053
	150	2.212		44	2.326	
NO_3^-	18	2.320	−0.110	0	2.302	0.045
	200	2.210		44	2.347	
ClO_4^-	18	2.207	−0.024	0	2.222	0.040
	150	2.183		44	2.262	
Br^-	18	2.283	−0.026	0	2.300	0.039
	150	2.257		44	2.339	
I^-	18	2.237	−0.030	0	2.222	0.020
	150	2.207		44	2.242	
$^1/_2$ $CdBr_4^{2-}$	20	2.232	−0.031	0	2.235	0.031
	150	2.201		40	2.266	
AgI_2^-	20	2.212	−0.029	0	2.193	0.029
	150	2.183		40	2.222	
			Cu(C,C-Me$_2$en)$_2$X$_2$			
NO_3^-	18	1.908	−0.39	0	1.923	0.038
	150	1.869		44	1.961	

[a] LT = low temperature, HT = high temperature, and

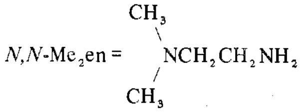


$C,C\text{-Me}_2\text{en} = H_2N\text{—}C(CH_3)_2\text{—}CH_2NH_2$

Table II. Comparison of Temperature and Pressure Effects on the Electronic Transitions of Ni(N,N-Me$_2$en)$_2$X$_2$ Thermochromic Complexes[a]

X^- in Ni(N,N-Me$_2$en)$_2$X$_2$	T, °C	Max abs, µm^{-1}	Δ_{abs}(LT–HT), µm^{-1}	Pressure (25 °C), kbar	Max abs, µm^{-1}	Δ_{abs}(40–0 kbar), µm^{-1}
BF_4^-	19	2.150	−0.031	0	2.174	0.048
	140	2.119		40	2.222	
ClO_4^-	19	2.183	−0.033	0	2.186	0.036
	140	2.150		40	2.222	
$^1/_2$ $CdBr_4^{2-}$	19	2.132	−0.031	0	2.139	0.023
	140	2.101		40	2.162	
$^1/_2$ HgI_4^{2-}	19	2.155	−0.036	0	Shifts into charge-transfer band with pressure	
	140	2.119		40		
I^-	20	2.150	−0.050	0	2.151	0.018
	140	2.075		40	2.169	

[a] LT = low temperature, HT = high temperature, and



$N,N\text{-Me}_2\text{en} = (CH_3)_2NCH_2CH_2NH_2$

dominant factor involved in the thermochromism. In an effort to see to what extent similar considerations hold for complexes involving other diamines (where presumed steric effects with temperature and pressure could be different), the nickel complexes of C,C-dimethylethylenediamine (C,C-Me$_2$en) and N,N-dimethylethylenediamine (N,N-Me$_2$en) were synthesized and investigated. The results of this study are reported in this note.

The results of the effects of temperature and pressure on the electronic transitions of complexes of the type Ni(C,C-Me$_2$en)$_2$X$_2$ and Ni(N,N-Me$_2$en)$_2$X$_2$ are tabulated in Tables I and II. These complexes are considered to be tetragonal with two long axial bonds along the fourfold axis. The effects of temperature are seen to shift the electronic transition toward lower frequencies. The effects of pressure are observed to be opposite in direction, blue shifts occurring. Similar results were obtained for the Et$_2$en complexes.[8] Steric effects are expected to be different for the complexes involving the three diamines. Thus, it is concluded that at least with diamines involving alkyl groups of the bulk of ethyl or methyl, steric factors are minimal, and the chief mechanism determining thermochromism in these complexes is the Lever effect. An increase in temperature causes the equatorial interactions to decrease with a simultaneous increase in axial interactions. With an increase in pressure the reverse occurs; the equatorial interactions increase while the axial interactions decrease. One may infer that although the pressure application affects these complexes in three directions, the effect along the MN$_4$ plane must be greater than along the axial positions. If the reverse were true, we should observe red shifts with pressure. Anisotropic pressure effects on noncubic crystals have been previously observed.[9,10] Drickamer[9] has found the pressure dependence of the a_0 and c_0 axes in tetragonal solids using x-ray diffraction. As one axis expands (c_0) with application of pressure, the other axis (a_0) contracts.

It may be observed from Tables I and II that an anion effect on the "d–d" transitions exists as pressures are increased. A decrease in the high-energy shifts (blue) with pressure occurs. The more polarizable or softer[11] anions show a smaller blue shift. Results are similar to those obtained for Et_2en,[8] although of smaller magnitude.

Experimental Section

Preparation. The amine ligands *N,N*-Me_2en and *C,C*-Me_2en were commercially obtained (Fluka) and were purified by distillation. The complexes were prepared according to procedure by Goodgame and Venanzi.[12] The complexes containing halometalates as anions were obtained by the method of Fabbrizzi et al.[7] Analyses gave satisfactory results.

Spectral Measurements. Electronic spectra under high external pressure were obtained in a diamond anvil cell[13] using a Cary 14 spectrophotometer interfaced with a special beam condenser.[14] The spectra at elevated temperatures were recorded with a Beckman DK-2A spectrophotometer. The complexes were spread on a filter paper and maintained in a thermostated cell. The temperature was controlled by a calibrated thermistor.

Registry No. Ni(*C,C*-$Me_2en)_2(BF_4)_2$, 62682-83-1; Ni(*C,C*-$Me_2en)_2(NO_3)_2$, 62682-85-3; Ni(*C,C*-$Me_2en)_2(ClO)_2$, 62682-84-2; Ni(*C,C*-$Me_2en)_2Br_2$, 19502-59-1; Ni(*C,C*-$Me_2en)_2I_2$, 19502-60-4; Ni(*C,C*-$Me_2en)_2CdBr_4$, 62669-54-9; Ni(*C,C*-$Me_2en)_2(AgI_2)_2$, 62669-53-8; Cu(*C,C*-$Me_2en)_2(NO_3)_2$, 62669-52-7; Ni(*N,N*-$Me_2en)_2(BF_4)_2$, 62669-55-0; Ni(*N,N*-$Me_2en)_2(ClO_4)_2$, 55326-15-3; Ni(*N,N*-$Me_2en)_2CdBr_4$, 62669-57-2; Ni(*N,N*-$Me_2en)_2HgI_4$, 62669-58-3; Ni(*N,N*-$Me_2en)_2I_2$, 62669-56-1.

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Structural Studies of Precursor and Partially Oxidized Conducting Salts. 12. Crystal Structure of $Rb_2[Pt(CN)_4](FHF)_{0.40}$. A New Lower Limit for the Platinum–Platinum Separation and the First Anhydrous One-Dimensional Tetracyanoplatinate Complex[1]

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It has been postulated[3,4] that the Peierls transition from a metallic to a low-temperature insulating state in one-dimensional conductors can be suppressed by increasing the interchain coupling. One method for testing these theoretical predictions involves the preparation of a series of similar materials in which the one-dimensional properties are preserved and the effects of various modifications can be investigated. This has been successful to some extent in the study of TTF–TCNQ and its many analogues.[5a] However, numerous attempts to prepare partially oxidized tetracyanoplatinate (POTCP) complexes,[5] of which $K_2[Pt(CN)_4]X_{0.3}\cdot 3H_2O$, X = Cl or Br, "KCP(X)", is the prototype, with anions other than Cl^- or Br^- have been unsuccessful. This is the case even for the simplest derivatives such as F^- or I^-.

Table I

Positional and Thermal Parameters for $Rb_2[Pt(CN)_4](FHF)_{0.40}$

Atom	x^a	y	z	B,[b] Å^2
Pt	0.0	0.0	0.0	*c*
C	0.0550 (8)	0.1480 (8)	0.0	*c*
N	0.0871 (8)	0.2325 (8)	0.0	*c*
Rb	0.1555 (3)	0.6555	0.0	*c*
F(1)	0.0	0.5	0.155 (14)	4.9 (11)
F(2)	0.0	0.5	0.25	5.7 (13)

Anisotropic Thermal Parameters (×10^4)[d]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	25.3 (5)	25.3	84 (2)	0	0	0
C	48 (7)	27 (5)	117 (29)	1 (5)	0	0
N	59 (7)	51 (7)	295 (40)	−15 (6)	0	0
Rb	72 (2)	72	382 (8)	27 (1)	0	0

[a] x, y, and z are fractional coordinates. [b] Isotropic temperature factor of the form $\exp(-B^2(\sin^2\theta)/\lambda^2)$. [c] Atoms refined anisotropically. [d] Anisotropic thermal parameters of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

In order to both prepare a new KCP(X) type derivative and, at the same time, increase interchain coupling (hopefully) through H-bonding interactions, we have synthesized an entirely new series of POTCP salts containing the triatomic bifluoride $(FHF)^-$ ion. These salts are most extraordinary and in this communication we wish to report the improved synthesis and the crystal structure of $Rb_2[Pt(CN)_4](FHF)_{0.40}$, RbCP(FHF), which has the shortest Pt–Pt distance (2.798 (1) Å) yet observed for any POTCP complex.

The preparation of RbCP(FHF) herein is slightly modified from that previously reported.[6] Needle-shaped crystals up to 5 mm in length were grown electrolytically from a 6 mL solution of 1.08 g of $Rb_2[Pt(CN)_4]\cdot 1.5H_2O$ to which 3 mL of concentrated HF and 2.0 g of RbF were added. The solution was electrolyzed at 1.5 V in a polyethylene beaker with Pt electrodes over a period of 24 h. The lustrous metallic gold-colored crystals were washed with cold water, and elemental analysis[7] indicated the formula to be $Rb_2[Pt(CN)_4](FHF)_{0.40}$ for the new material.

A 0.34 mm long crystal was cut (0.0036 mm^2 cross section) and was used for data collection on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. Intensity measurements were made in the θ–2θ step-scan mode using Mo Kα x radiation. Weissenberg photographs of the RbCP(FHF) crystals exhibited body-centered tetragonal $4/mmm$ Laue symmetry ($h + k + l = 2n$) with the additional systematic absences $l = 2n + 1$ for the $h0l$ and $0kl$ reflections. The centrosymmetric space group $I4/mcm$ (D_{4h}^{18}, No. 140) was chosen initially and was justified by the satisfactory least-squares refinement ultimately obtained. The refined cell parameters (12 diffractometer-centered reflections) are a = 12.689 (2) Å, c = 5.595 (1) Å, and V = 900.9 Å^3 with Z = 4 and a calculated density of 3.58 g/cm^3. The structure was solved by a combination of direct methods, least-squares, and Fourier synthesis procedures to yield final agreement factors of $R(F_o) = 0.045$, $R(F_o^2) = 0.053$, and $R_w(F_o^2) = 0.070$ based on 383 independent reflections corrected for absorption (μ = 278.66 cm^{-1}). The final positional and thermal parameters are presented in Table I.

The crystal structure, as shown in Figure 1, consists of columnar chains of square-planar $Pt(CN)_4^{-1.60}$ groups which