(cyclopentylamine)(dimethyl sulfoxido)platinum(II), 50830-88-1; *cis*-dichloro(cyclohexylamine)(dimethyl sulfoxido)platinum(II), 50830-89-2; *cis*-dichloro(cycloheptylamine)(dimethyl sulfoxido)platinum(II), 50830-90-5; *cis*-dichloro(cyclooctylamine)(dimethyl sulfoxido)platinum(II), 50830-91-6; dichlorobis(dimethyl sulfoxido)platinum(II), 15274-33-6.

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Anion-Cation Interaction in Tetrakis(alkyl isocyanide)platinum(II) Tetracyanoplatinate(II) Double Complexes in the Solid State and in Solution[1]

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Three double-complex salts $[Pt(CNR)_4][Pt(CN)_4]$ ($R = CH_3$, C_2H_5, or $t\text{-}C_4H_9$) exhibit low-energy electronic absorption bands in the solids (at 22.25 and 22.30 kK for the methyl and ethyl compounds, respectively, in KBr pellets and at 17.70 kK for the *tert*-butyl compound in a Nujol mull) which are absent in the solution spectra of the anion or cation complexes with simple counterions. These low-energy bands, which are responsible for the intense colors of the solids, are ascribed to metal → ligand charge transfer which has been red shifted by Davydov interaction between anion and cation complexes in the solid lattice. The ethyl and *tert*-butyl compounds are also slightly soluble in acetonitrile, and the ethyl compound is slightly soluble in water and ethanol. These solutions exhibit a low-energy band near 30 kK which is also absent in anion or cation spectra. The concentration dependence of the solution spectra does not obey Beer's law, and the solution conductance is lower than expected for 1:1 electrolytes. These results are interpreted in terms of an anion-cation association equilibrium. Association constants in acetonitrile at 24° were found to be $(4.0 \pm 0.5) \times 10^4\ M^{-1}$ for $Pt(CNC_2H_5)_4^{2+}$ and $Pt(CN)_4^{2-}$ from spectrophotometric and conductance data and $(2.0 \pm 0.5) \times 10^5\ M^{-1}$ for $Pt(CN\text{-}t\text{-}C_4H_9)_4^{2+}$ and $Pt(CN)_4^{2-}$ from spectrophotometric data. A model is proposed for the structure of the associated complex, and the origin of the low-energy absorption is discussed.

Introduction

Double-complex salts of the type $[PtA_4][PtX_4]$ consisting of square-planar cations and square-planar anions of equal ionic charges are fairly common in platinum(II) chemistry, and numerous examples have been known for many years.[2] One of the most notable examples of such a salt is green $[Pt(NH_3)_4][PtCl_4]$, first reported by Magnus in 1828[3] and commonly called Magnus' green salt (MGS). Solid MGS has intrigued investigators for years because its color is "abnormal," since it is not like that of either the cation (colorless) or the anion (red) complexes with simple counterions.[4] The abnormal color and also anisotropic electrical conductivity of the solid reported recently[5] are believed due to a structural feature of the crystal which allows anion-cation interaction. The structure[6] of MGS consists of an infinite stack of alternating planar cations and anions along the crystal *c* axis forming a chain with uniform Pt-Pt distances of 3.24 Å. The color of MGS results from a strong solid-state perturbation of the $PtCl_4^{2-}$ ligand field spectra, causing a red shift of the $^1A_{1g} \rightarrow {}^{1,3}E_g$ ligand-field transitions by about 4000 cm^{-1}, leaving a "window" near 20 kK in the green region of the spectrum.[4] Numerous other related double-complex salts of platinum(II) have structures which are similar to, if not isomorphous with, that of MGS; Pt-Pt distances along the chain direction range from 3.2 to 3.6 Å.[7] The colors of the solids and other features of their electronic spectra are related to the anion-cation Pt-Pt distance.

Nearly all of these double-complex salts, including MGS, are highly insoluble. Consequently anion-cation interaction phenomena have been investigated only in the solid state. In the present paper we report the preparation and characterization of three tetrakis(alkyl isocyanide)platinum(II) tetracyanoplatinate(II) double-complex salts, $[Pt(CNR)_4][Pt(CN)_4]$ ($R = CH_3$, C_2H_5, or $t\text{-}C_4H_9$), two of which ($R = C_2H_5$ or $t\text{-}C_4H_9$) show a low but definite solubility in acetonitrile; the ethyl compound is also slightly soluble in water and ethanol. Thus in addition to spectral measurements on the solid salts, the solution properties of the two salts were investigated, and evidence is presented for anion-cation interaction in solution.

Experimental Section

Preparation of Compounds. The starting material for the double complex salts was potassium tetracyanoplatinate(II), $K_2[Pt(CN)_4]$, which was prepared by the literature method[8] and converted to the *n*-butylammonium salt.[9] The complex $[Pt(CNC_2H_5)_4][BF_4]_2$ was prepared by alkylating $Pt(CN)_4^{2-}$ with triethyloxonium tetrafluoroborate according to the method described for the methyl compound.[10] A sample of $[Pt(CNCH_3)_4][BF_4]_2$ was kindly supplied by Professor P. M. Treichel.[10] The *tert*-butyl isocyanide ligand was prepared and purified according to the method of Casanova, *et al.*[11] Tetra-*n*-butylammonium tetrachloroplatinate(II) was prepared as described previously.[9] All other chemicals were reagent grade; solvents were Spectro Grade and were used without further purification.

Tetrakis(ethyl isocyanide)platinum(II) Tetracyanoplatinate(II),

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[1] Taken in part from the Ph.D. dissertation of H. I., Northern Illinois University, DeKalb, Ill., 1974.

[2] See for example "Gmelins Handbuch der anorganischen Chemie," Vol. 68D, 8th ed, Verlag Chemie, Weinheim/Bergstr., Germany, 1957.

[3] G. Magnus, *Pogg. Ann.*, 14, 239 (1828), cited in ref 2.

[4] D. S. Martin, Jr., R. M. Rush, R. F. Kroening, and P. E. Fanwick, *Inorg. Chem.*, 12, 301 (1973), and references cited therein.

[5] A. E. Underhill, P. S. Gomms, and T. W. Thomas, *J. Chem. Soc. A*, 2154 (1971).

[6] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 79, 3017 (1957).

[7] J. R. Miller, *J. Chem. Soc.*, 4452 (1961); *Advan. Inorg. Chem. Radiochem.*, 4, 133 (1962).

[8] Reference 2, Vol. 68C, p 202.

[9] W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5721 (1968).

[10] P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.*, 93, 5424 (1971).

[11] J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, 31, 3473 (1966).

$[Pt(CNC_2H_5)_4][Pt(CN)_4]$, and Tetrakis(methyl isocyanide)platinum(II) Tetracyanoplatinate(II), $[Pt(CNCH_3)_4][Pt(CN)_4]$. Equal numbers of moles of $[Pt(CNR)_4][BF_4]_2$ and $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ were dissolved in separate dichloromethane solutions, and these solutions were mixed slowly with stirring. Bright yellow, fluorescent crystalline solids were immediately formed; these were collected by suction filtration, washed with excess dichloromethane and anhydrous ether, and dried *in vacuo* overnight at room temperature (yield 90%). *Anal.* Calcd for $[Pt(CNC_2H_5)_4][Pt(CN)_4]$: C, 26.89; H, 2.82; N, 15.68; Pt, 54.60. Found: C, 27.05; H, 2.87; N, 15.73; Pt, 54.56. Calcd for $[Pt(CNCH_3)_4][Pt(CN)_4]$: C, 21.88; H, 1.82; N, 17.02; Pt, 59.28. Found: C, 21.58; H, 1.87; N, 16.90; Pt, 59.09. Ir: $[Pt(CNC_2H_5)_4][Pt(CN)_4]$, $\bar{\nu}_{CN}(CNC_2H_5)$ 2290 cm^{-1}, $\bar{\nu}_{CN}(CN^-)$ 2138 cm^{-1}; $[Pt(CNCH_3)_4][Pt(CN)_4]$, $\nu_{CN}(CNCH_3)$ 2308 cm^{-1}, $\nu_{CN}(CN^-)$ 2136 cm^{-1}.

Tetrakis(*tert*-butyl isocyanide)platinum(II) Tetracyanoplatinate(II), $[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$.[12] A fourfold excess of *tert*-butyl isocyanide was added dropwise to a dichloromethane solution containing equimolar amounts of $[(n\text{-}C_4H_9)_4N]_2[PtCl_4]$ and $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$. About 5 min after the ligand had been added, a precipitate was formed, and the resulting mixture was stirred for 4 hr and cooled in an ice bath. A green crystalline solid was collected, washed with cold dichloromethane and anhydrous ether, and dried *in vacuo* (yield 72%). *Anal.* Calcd for $[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$: C, 34.86; H, 4.39; N, 13.55; Pt, 47.19. Found: C, 34.21; H, 4.24; N, 13.43; Pt, 47.29. Ir: $\bar{\nu}_{CN}(CN\text{-}t\text{-}C_4H_9)$ 2280 cm^{-1}, $\bar{\nu}_{CN}(CN^-)$ 2132 cm^{-1}.

Spectral and Conductance Measurements. Infrared spectra were obtained using either potassium bromide pellets or Nujol mulls spread between cesium iodide plates and a Beckman IR-12 spectrophotometer. Electronic spectra were obtained using a Cary 1501 spectrophotometer. Solid-state spectra were determined from samples pressed in potassium bromide pellets or by using a Nujol mull spread on tissue paper. Solution spectra were obtained using 1-cm quartz cells. All spectral measurements were made at room temperature. Conductance measurements were made using a bipolar current conductivity apparatus as described by Daum and Nelson[13] and a conductivity cell of known cell constant.

Anion–Cation Association Constants. Spectrophotometric studies showed that absorbance *vs.* concentration data do not follow Beer's law for the ethyl compound over the concentration range 10^{-4}–10^{-5} *M* or the *tert*-butyl compound over the concentration range (1–5) × 10^{-5} *M* in acetonitrile solutions. This behavior is attributed to anion–cation association in solution. Association constants were determined from eq 1 [C = stoichiometric concentra-

$$C/A^{1/2} = A^{1/2}/\epsilon + (K\epsilon)^{-1/2} \tag{1}$$

tion of the double complex, A = measured absorbance at 29.8 kK for the ethyl compound or 29.3 kK for the *tert*-butyl compound, ϵ = molar absorptivity at the energy of the absorbance measurement ($1.54 \times 10^4\ M^{-1}\ cm^{-1}$ at 29.8 kK for the ethyl compound or $1.81 \times 10^4\ M^{-1}\ cm^{-1}$ at 29.3 kK for the *tert*-butyl compound), and K = anion-cation association constant]. The derivation of eq 1 is straightforward and assumes that 1-cm^{-1} cells are used and that the absorption at 29.8 or 29.3 kK is due only to the associated complex. Plots of $C/A^{1/2}$ *vs.* $A^{1/2}$ were linear, and the slope gave the value of ϵ. Values of K for the ethyl compound calculated for eight different concentrations were self-consistent to within ±8%, while values calculated from four concentrations of the *tert*-butyl compound were self-consistent to within ±16%.

Conductance measurements on solutions of the double complexes showed that the conductivity was less than expected for a 1:1 electrolyte. The Ostwald dilution law, eq 2, was applied to

$$K = (1 - \alpha)/C\alpha^2 \tag{2}$$

some data collected for the ethyl compound in acetonitrile. In eq 2, $\alpha = \Lambda_c/\Lambda_\infty$, and C and K have the same meaning as in eq 1; Λ_c and Λ_∞ are equivalent conductances at concentration C and at infinite dilution, respectively. The equivalent conductance at infinite dilution was determined by extrapolation of a linear plot of Λ_c *vs.* $C^{1/2}$ (C in equivalents per liter) to zero concentration. Values of K were self-consistent to within ±7% for six concentrations over the range (1–4) × 10^{-5} *M*. Some measurements at higher concentrations gave slightly higher values of K, probably because of inadequacy of the dilution law as the per cent association became quite high (50–70% associated). Conductance data as a function of concentration were not collected for the *tert*-butyl compound because marked changes were noted in the spectra in the times required for the conductance measurements.

Results and Discussion

Solid Double-Complex Salts. The three solid salts $[Pt(CNR)_4][Pt(CN)_4]$ ($R = CH_3$, C_2H_5, $t\text{-}C_4H_9$) were each characterized by complete elemental analysis and infrared and electronic spectra. The solid salts resemble MGS and other related $[PtA_4][PtX_4]$ double complexes of platinum(II) in several respects. They are easily formed on mixing solutions of anion and cation, they are characterized by low solubility compared to the anion or cation complexes with simple counterions, and their colors differ from either the anion or cation complex. It is probable that the alkyl isocyanide–cyano double-complex salts described here have lattice structures similar to the alternating anion–cation chain structure of MGS. A fair number of double-complex salts of platinum(II) adopt this basic type of solid lattice or a very closely related variant.[7] To lend support to this suggestion, an X-ray powder pattern was obtained for the ethyl compound. A very clear pattern was observed, and the most intense lines resulting from the platinum atom scattering were satisfactorily indexed in terms of a tetragonal cell with $a = b = 9.23$ Å and $c = 3.34$ Å.[14] Comparable dimensions of the MGS lattice, which is also tetragonal, are $a = b = 9.03$ Å and $c/2 = 3.25$ Å.

Since neither the $Pt(CNR)_4^{2+}$ cations nor the $Pt(CN)_4^{2-}$ anions show appreciable absorption at energies lower than 35 kK in solution, the intense colors of the double complex salts are a striking feature. Figure 1 presents the electronic spectrum of solid $[Pt(CNC_2H_5)_4][Pt(CN)_4]$ in a pressed KBr pellet. Results for the methyl compound were quite similar, but the *tert*-butyl compound changed color from green to red on forming the KBr pellet, indicating either a radical change in lattice structure or a decomposition of the compound. However, satisfactory solid spectra for the green *tert*-butyl compound were obtained using a Nujol mull. Spectral data for the double-complex salts are collected in Table I; some solution spectral data for the $Pt(CNR)_4^{2+}$ and $Pt(CN)_4^{2-}$ complexes are included for comparison. For all three of the double-complex salts the intense color of the solid is due to a prominent absorption band in the visible spectra which is completely absent in the solution spectra of the anion or cation complexes. These strong low-energy bands must arise as a result of the collective nature of the lattice. Figure 1 also shows several somewhat weaker absorption bands at higher energy. The positions of these bands are rather similar in energy to bands observed in the solution spectra of the anion and cation complexes.

The interpretation of the spectra of the solid double-complex salts logically begins with the spectral features of the anion and cation complexes. The solution spectra of the $Pt(CN)_4^{2-}$ anion and the $Pt(CNR)_4^{2+}$ cations are remarkably similar, showing several intense bands in the region 35–50 kK. For $Pt(CN)_4^{2-}$ these bands have been assigned to charge-transfer transitions of the metal → ligand (M → L) type;[9,15] the similarity of the bands observed for the Pt-

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(12) This compound has been described by Malatesta and Bonati (L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, New York, N. Y., 1969, p 169), but we were unable to reproduce their preparative method involving reaction of $t\text{-}C_4H_9\text{-}NC$ with $Pt(CN)_4^{2-}$.

(13) P. H. Daum and D. F. Nelson, *Anal. Chem.*, **45**, 463 (1973).

(14) The authors are indebted to Dr. H. B. Krause, Department of Physics, Northern Illinois University, for making the X-ray measurements and indexing the powder pattern.

(15) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Amer. Chem. Soc.*, **91**, 5994 (1969).

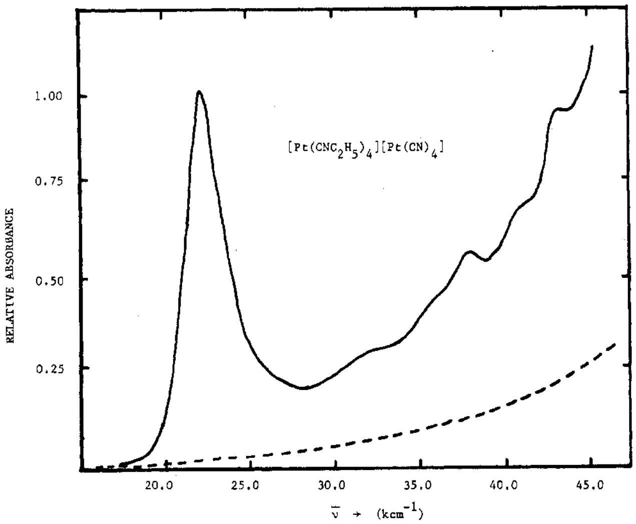

Figure 1. Electronic spectra of $[Pt(CNC_2H_5)_4][Pt(CN)_4]$ in a pressed potassium bromide pellet (solid line). Background absorption due to potassium bromide (dashed line).

Table I. Spectral Data for $[Pt(CNR)_4][Pt(CN)_4]$ Double-Complex Salts and Related Complexes

$\bar{\nu}$, kK (rel abs)

$[Pt(CNCH_3)_4][Pt(CN)_4]$	$[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$	
Solid[a]	Solid[b]	CH_3CN soln[c,d]
22.25 (0.96)	17.70 (0.89)	29.25 (0.35)
31.50 (0.22)[e]	30.40 (0.30)	36.25 (0.16)[e]
35.00 (0.39)[e]	34.50 (0.40)	38.70 (0.27)
37.50 (0.61)	41.00 (0.55)	42.00 (0.34)[e]
41.00 (0.59)[e]	43.70 (0.71)	45.60 (0.83)
43.00 (0.84)[e]	49.30 (1.00)	47.75 (0.76)[e]
45.00 (1.00)[e]		50.50 (1.00)

$\bar{\nu}$, kK (rel abs)

$[Pt(CNC_2H_5)_4][Pt(CN)_4]$			
	Soln		
Solid[a]	CH_3CN[c,f]	Water[c,g]	Ethanol[c,d]
22.30 (1.00)	29.70 (0.55)	27.70 (0.40)	29.80 (0.54)
32.00 (0.30)[e]	36.00 (0.27)[e]	31.60 (0.83)	39.00 (0.30)
36.00 (0.44)[e]	38.35 (0.42)	36.00 (0.30)	42.50 (0.54)[e]
37.70 (0.56)	41.70 (0.43)	39.40 (0.89)	46.00 (1.00)[e]
41.00 (0.69)	45.60 (1.00)	41.75 (0.80)[e]	
43.00 (0.68)	48.00 (0.89)	43.00 (1.00)	
		46.50 (>1.9)	
		47.80 (>1.9)	

CH_3CN Soln $\bar{\nu}$, kK (ϵ, M^{-1} cm^{-1})

$[Pt(CNCH_3)_4]\cdot[BF_4]_2$	$[Pt(CNC_2H_5)_4]\cdot[BF_4]_2$	$[(n\text{-}C_4H_9)_4N]_2\cdot[Pt(CN)_4]$
36.75 (2080)	36.70 (2670)	35.40 (1230)
39.40 (7490)	39.35 (8550)	38.45 (12,900)
41.65 (7060)	41.45 (8880)	40.50 (1840)[e]
43.70 (3400)	43.50 (4270)	45.50 (29,300)
46.50 (6350)[e]	46.25 (7950)	47.00 (8780)[e]
48.70 (18,600)	48.25 (22,000)	

[a] KBr pellet. [b] Nujol Mull. [c] Beer's law not obeyed. [d] Determined for a saturated solution. [e] Shoulder. [f] Determined for 8.76 × 10^{-5} M in double complex. [g] Determined for 1.3 × 10^{-4} M in double complex.

$(CNR)_4^{2+}$ cations would indicate an assignment to M → L processes would also be appropriate. A simplified energy level diagram for these complexes is given in Figure 2, showing the spectroscopically important levels. The M → L transitions for the anion and cation complexes result from excitations from the occupied d_{xy}, $d_{xz}d_{yz}$, or d_{z^2} orbitals to the low-lying $a_{2u}(\pi^*)$ orbital of cyanide in the anion or alkyl isocyanide in the cation. A detailed interpretation of the anion and cation solution spectra is complicated by spin-orbit effects[15] and is not essential to the qualitative discussion to be presented here. A more complete treatment of the spectra of $Pt(CN)_4^{2-}$, $Pt(CNR)_4^{2+}$, and related complexes is the subject of a forthcoming paper, but for the present discussion attention will be focused on the "new" absorption bands which arise as a result of lattice formation. These bands are assigned as "perturbed" M → L charge-transfer transition(s) of the anion and cation shifted to lower energy by specific interactions between anions and cations in the crystal. The low-lying excited states of the solid reached by these transitions can be described in terms of an exciton model.[16] Exciton theory has been successful in the interpretation of spectra of solid aromatic compounds in organic chemistry, and it has been applied recently to the interpretation of crystal spectra of $Pt(en)Cl_2$ by Martin and coworkers.[17]

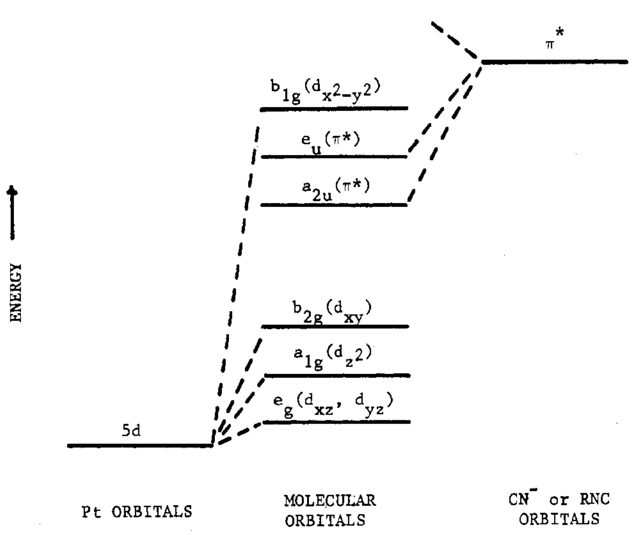

Figure 2. Simplified energy level diagram for $Pt(CN)_4^{2-}$ or $Pt(CNR)_4^{2+}$ complexes. The highest occupied orbital is $b_{2g}(xy)$, and the ground state is diamagnetic and designated $^1A_{1g}$.

Following the treatment outlined by Martin, *et al.*,[17] if it is assumed that the anion and cation have essentially the same molecular excited states and that there are a single anion and cation in a unit cell (or primitive cell) and there is a uniform spacing between anions and cations in the chain along the crystal *c* direction, then a Davydov splitting of each corresponding excited state of the anion and cation into a pair of states is expected. However since the molecular axes in the solid are visualized as being aligned in a parallel manner along the chain axis and the intramolecular excitations of the anion and cation are the same, the intensity of the transition to one of the Davydov states will be very low. Thus for corresponding dipole-allowed M → L transitions of the anion and cation complexes, a single transition of appreciable intensity is expected in the solid, but the transition will be shifted in energy from the transitions in the isolated complexes. The transition energy in the solid will have the form given in eq 3, where $\bar{\nu}^0_{i\to j}$ is the transition

$$\bar{\nu}_{i\to j} = \bar{\nu}^0_{i\to j} + D + I \qquad (3)$$

energy for the isolated complexes, D is difference in van der Waals energy between ground and excited states, and I

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(16) D. P. Craig and S. H. Walmsley, "Excitons in Molecular Crystals," W. A. Benjamin, New York, N. Y., 1968.

(17) D. S. Martin, Jr., L. D. Hunter, R. Kroening, and R. F. Coley, *J. Amer. Chem. Soc.*, 93, 5433 (1971).

describes the Davydov splitting. The quantity D is expected to be negative (causing a red shift) since excited states are visualized as being larger and able to interact more effectively at longer distances than the ground state. A dipole-dipole approximation of I for a set of molecular axes which places the z axis between adjacent molecules and the x and y axes orthogonal to z is given in eq 4 for dipole-allowed transitions

$$I = \sum_{\mathrm{n} \neq \mathrm{m}} I_{\mathrm{nm}} = \sum_{\mathrm{n} \neq \mathrm{m}} e^2 R_{\mathrm{nm}}^{-3}(x_{\mathrm{n}}x_{\mathrm{m}} + y_{\mathrm{n}}y_{\mathrm{m}} - 2z_{\mathrm{n}}z_{\mathrm{m}}) \qquad (4)$$

with transition moments $e\mathbf{r}$. In eq 4, x_{n} is the x component of the transition moment on molecule n, etc., and R_{nm} is the distance between n and m, taken in the present case to be the anion-cation distance along the chain. The form of eq 4 is such that for transitions polarized along the z axis or chain direction (crystal c axis), I will be negative and the z-polarized transition will shift to lower energy, while for transitions polarized in the x,y direction, I will be positive and the shift will be to higher energy. Thus for a z-polarized transition, the contributions to the shift from D and I are both negative, and a substantial red shift would be anticipated. For an x,y-polarized transition, the contributions from D and I are of opposite sign, and thus the shift is dependent upon their relative magnitudes. Therefore, it is proposed that the intense low-energy bands observed in the solid double-complex salts are z-polarized M → L charge-transfer transitions red shifted by 16–24 kK in the case of the methyl or ethyl compounds or by 20–28 kK for the *tert*-butyl compound. It is probable that the M → L charge transfer arises from the $d_{z^2} \rightarrow a_{2u}(\pi^*)$ excitation of the anion and cation complexes, which is designated ${}^1A_{1g} \rightarrow {}^1A_{2u}$ and is fully allowed in the z polarization. In solution this transition is believed to be near 46 kK in $Pt(CN)_4^{2-}$ and 46–48 kK in $Pt(CNR)_4^{2+}$, but these excited states are strongly mixed with lower energy states *via* spin-orbit coupling.[15] The bands which are observed at higher energy in the solid double complex salts, which are only slightly shifted from solution energies, are likely due to the in-plane x,y-polarized transitions. If this assignment is correct, then the magnitudes of I and D are similar.

In the absence of complete structural data, it is difficult to estimate the magnitude of the shifts expected, but a shift of about −12 kK was estimated for the z-polarized ligand → metal charge transfer in $Pt(en)Cl_2$, which also adopts a chain-type structure with a Pt-Pt distance of 3.39 Å.[17] It is interesting that the shift to lower energy is larger for the *tert*-butyl compound than for the methyl or ethyl. This may be an indication of a shorter Pt-Pt distance in the solid, but in the absence of structural information on this compound, to suggest reasons for this would be speculative. Also the polarizations of the intense solid-state bands are not known. Such information could support the interpretation advanced here.

Solution Spectra and Evidence for Anion–Cation Association. Both the ethyl and *tert*-butyl double-complex salts have a low but definite solubility in acetonitrile. The ethyl compound is also slightly soluble in water and alcohol. The methyl compound was insoluble. The solubility of the ethyl compound in acetonitrile at 24° was found to be (1.0–1.1) × 10^{-4} M in double-complex salt, while the solubility of the *tert*-butyl compound was (0.4–0.5) × 10^{-4} M. Acetonitrile solutions of the ethyl compound were fairly stable with little change in the electronic spectra being observed for periods up to 15 min, but at longer times (1-3 hr) gradual changes in the spectra were noted. Acetonitrile solutions of the *tert*-butyl compound and water or ethanol solutions of the ethyl compound were less stable, and changes in their spectra were noted within a few minutes of dissolution of the solid salts. Consequently the bulk of our investigations involved acetonitrile solutions of the ethyl compound, and measurements were made within minutes of dissolution of the salt.

Figure 3 presents the spectra of the $[Pt(CNC_2H_5)_4][Pt(CN)_4]$ salt in acetonitrile; included also in Figure 3 is a sketch of a superposition of spectra of $[Pt(CNC_2H_5)_4][BF_4]_2$ and spectra of $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ determined separately in acetonitrile. An intense band appears near 30 kK in the solution spectra of the double complex salt which is absent in the spectra of the anion or cation complexes. The higher energy portion of the spectra contains bands which compare favorably with the positions of bands in the superposition of anion and cation spectra. However, it was found that the concentration dependence of both the 30-kK band and the higher energy portion of the solution spectra of the double-complex salt do not follow Beer's law. With increasing concentration, the 30-kK band appeared relatively more intense, and the higher energy portion resembling the superposition of anion and cation spectra became relatively less intense. The solution spectra of the *tert*-butyl compound in acetonitrile behaved similarly; qualitatively so did the solutions of the ethyl compound in water or ethanol. In each case the low-energy band appeared near 30 kK. It is important to note also that the solution spectra obtained for the ethyl double-complex salt were identical with spectra obtained on mixing dilute solutions of $[Pt(CNC_2H_5)_4][BF_4]_2$ and $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$, provided concentrations were below the double-complex salt solubility limit. Spectral data from the solution measurements are collected in Table I.

Both the appearance of the 30-kK band and the failure of Beer's law for the solution spectra of the double complex salts can be interpreted in terms of an equilibrium involving anion–cation association in solution. This association, described in eq 5, is visualized as forming a zero-charged

$$Pt(CNR)_4^{2+} + Pt(CN)_4^{2-} \overset{K}{\rightleftharpoons} [Pt(CNR)_4 \cdots Pt(CN)_4]^0 \qquad (5)$$

anion–cation complex in which there is a significant perturbation of the spectroscopically important energy levels of the two complexes giving rise to the "new" 30-kK absorption.

If it is assumed that the 30-kK band in the solution spectra is a property of the associated anion–cation complex of eq 5 and that its intensity is linearly dependent on the concentration of the associated complex, then a value for the association constant K can be obtained from absorbance *vs.* concentration data. Such data for the ethyl and *tert*-butyl compounds in acetonitrile at 24° and the calculated values of K are given in Table II. The presence of unassociated anion and cation complexes in solution would explain the close correspondence of band positions between the double-complex salt solutions and the superposition of anion and cation spectra.[18] The existence of the equilibrium eq 5

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[18] The value of K for the ethyl compound indicates that even at the highest concentration studied (~10^{-4} M), about 39% of the anion and cation concentration remains unassociated. Thus the spectra due to the associated complex above 35 kK could not be determined accurately. However, the difference between the observed spectra of the double-complex salt and that expected for the free anion and cation at equilibrium did reveal several rather ill-defined bands in the energy region 34–50 kK with absorptivities <10,000 M^{-1} cm^{-1}. This absorption is likely due to transitions which are largely intraionic and polarized in the molecular planes of the anion and cation complexes (see text below), but further comment on this absorption would be speculative in view of the reliability of the data.

Table II. Association Constants for $Pt(CNR)_4{}^{2+}$ and $Pt(CN)_4{}^{2-}$ in Acetonitrile at 24°

A. By Spectrophotometry

10^5 [double complex], M	Absorbance	$10^{-4}K$,[a] M^{-1}
	$[Pt(CNC_2H_5)_4][Pt(CN)_4]$[b]	
3.00	0.200	4.5
4.45	0.316	3.6
5.85	0.477	4.1
6.63	0.561	4.1
7.84	0.670	3.6
8.76	0.774	3.6
9.68	0.908	4.1
10.2	0.980	4.4
	$[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$[c]	
1.09	0.106	23
1.67	0.163	15
2.21	0.235	16
3.39	0.420	20

B. By Conductivity

10^5 [double complex], M	Λ_c, cm^2 ohm^{-1} equiv^{-1}	α[d]	$10^{-4}K$,[e] M^{-1}
	$[Pt(CNC_2H_5)_4][Pt(CN)_4]$		
1.15	85.0	0.739	4.1
1.28	84.5	0.735	3.8
1.76	79.5	0.691	3.7
2.40	72.5	0.630	3.9
2.92	67.5	0.587	4.1
3.71	62.0	0.539	4.3

[a] Calculated from eq 1. [b] Measurements made at 29.7 kK; ϵ(29.7 kK) 1.54×10^4 M^{-1} cm^{-1}. [c] Measurements made at 29.2 kK; ϵ(29.2 kK) 1.81×10^4 M^{-1} cm^{-1}. [d] Degree of dissociation = Λ_c/Λ_∞; $\Lambda_\infty = 115$ cm^2 ohm^{-1} equiv^{-1}. [e] Calculated from eq 2.

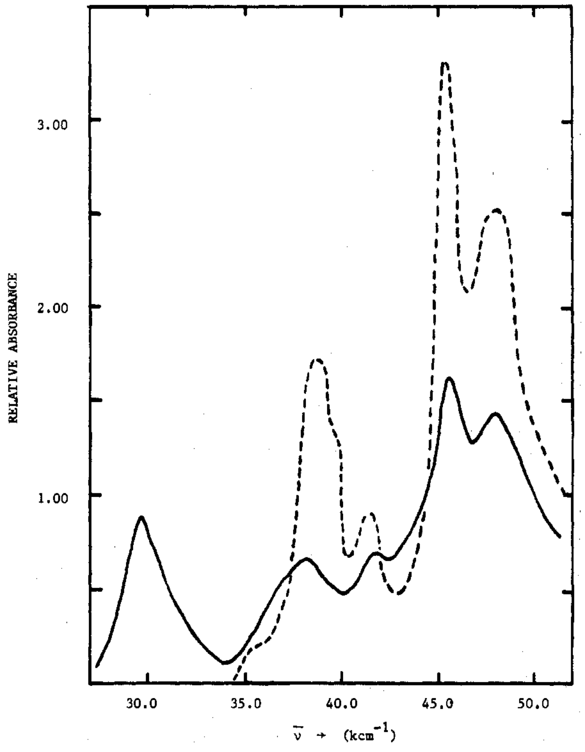


Figure 3. Electronic spectra of $[Pt(CNC_2H_5)_4][Pt(CN)_4]$ in acetonitrile solution (solid line); salt concentration 8.7×10^{-5} M. Superposition of spectra of $[Pt(CNC_2H_5)_4][BF_4]_2$ and $[(n\text{-}C_4H_9)_4N]_2$-$[Pt(CN)_4]$ determined separately in acetonitrile (dashed line); $[Pt(CNC_2H_5)_4{}^{2+}] = [Pt(CN)_4{}^{2-}] = 8.7 \times 10^{-5}$ M.

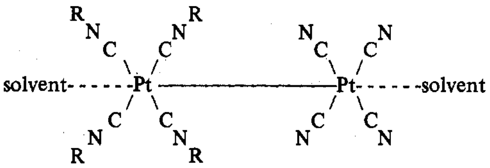
Table III. Conductance Data for $[Pt(CNR)_4][Pt(CN)_4]$ Double-Complex Salts and Related Complexes

Compd	Solvent	$10^5 \times$ conc, M	Molar conductance, cm^2 ohm^{-1} mol^{-1}
$[Pt(CNC_2H_5)_4][Pt(CN)_4]$	CH_3CN	8.2	77
	H_2O	7.5	142
$[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$	CH_3CN	2.0	110
$[Pt(CNC_2H_5)_4][BF_4]_2$	CH_3CN	8.5	410
	H_2O	10.7	256
$[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$	CH_3CN	8.8	359
	H_2O	9.8	244
$[(n\text{-}C_4H_9)_4N][BF_4]$	H_2O	10.7	137

would also explain the failure of Beer's law and at the same time rationalize the opposite concentration dependencies observed for the 30-kK band and the higher energy portion of the spectrum. There was no evidence for a greater association than a single anion-cation pair up to the highest concentrations investigated for both the ethyl and *tert*-butyl compounds.

The anion-cation association equilibrium predicts charge neutralization in proportion to the amount of the associated species present. Consequently, some conductance measurements were made on solutions of the double-complex salt. The results of these measurements showed that when conductances of the double-complex salt solutions were compared with conductances of solutions of anion or cation complexes with simple counterions, values were found that were lower than expected for a 1:1 electrolyte. Some conductance data are collected in Table III. For the ethyl compound in acetonitrile some conductance data as a function of concentration were obtained and a value of the association constant was calculated. These results are also included in Table II. The agreement with the constants determined by spectrophotometry is well within experimental error and thus quite encouraging.

Some comments on the nature of the associated anion-cation complex of eq 5 are in order. In view of the doubly charged $Pt(CN)_4{}^{2-}$ and $Pt(CNR)_4{}^{2+}$ complexes, it is not at all unreasonable to expect association in solution. Ion-pair formation would be anticipated even in the absence of specific interactions between anion and cation complexes. However the appearance of the 30-kK band indicates that specific interactions between the anion and cation do exist, and furthermore these interactions are sufficient to cause a significant perturbation of the anion and cation electronic spectra. In solution the most plausible direction for a significant perturbation in a planar complex would be along a line perpendicular to the molecular plane. Therefore a reasonable structure for the associated anion-cation complex which would allow for such axial perturbation is sketched in I. This structure in which the anion and cation molecular



I

planes are parallel, but of unspecified rotameric conformation, might be viewed as a solvated anion-cation unit of the solid lattice. A structure such as I can be used to interpret the origin of the 30-kK band in the solution spectra by constructing molecular orbitals of the associated complex from those of the isolated anion and cation complexes. The orbitals of the anion and cation complexes which would be expected to have the largest overlap in forming a pair complex of the type in I are those which are largely metal orbitals which are perpendicular to the molecular planes, *viz.*, d_{z^2} and p_z. Overlap of other orbitals is expected to be significantly smaller. An energy level diagram showing the interaction of the d_{z^2} and p_z metal orbitals and the spectroscopically important π^* combination of the cyanide and isocyanide ligands is given in Figure 4. The symmetry of I will be C_{4v} if the rotameric conformation is eclipsed or staggered; otherwise it will be C_4 as long as the molecular planes of the anion and cation complexes are parallel. The levels of Figure 4 are labeled according to C_{4v}, but those of C_4 would be equivalent. Since the combinations of the d_{z^2} orbitals and those of the p_z orbitals have the same symmetry, significant mixing of these levels may be visualized, and this mixing can impart stability to the anion-cation complex by lowering the energy of the occupied orbitals. The 30-kK band is interpreted as the transition $2a_1(d_{z^2}) \rightarrow 3a_1(\pi^*)$ $[^1A_1 \rightarrow {}^1A_1]$; this transition would be dipole allowed and polarized in the direction of the Pt-Pt axis in the associated complex.

It is interesting that the *tert*-butyl complex association constant is greater than for the ethyl compound. This may be an indication that the steric requirement for the alkyl group plays a minor role in affecting the stability of the anion-cation complex and that other factors such as inductive effects of the alkyl group or solvation differences may be more important.

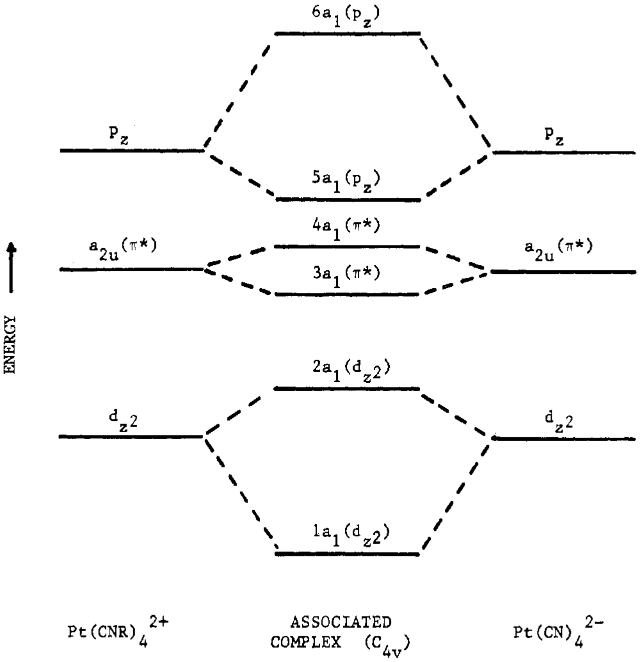


Figure 4. Energy levels of the anion-cation associated complex. Only the levels resulting from the interaction of d_{z^2} and p_z orbitals are shown along with the spectroscopically important π^* combinations from the cyanide and alkyl isocyanide ligands.

Registry No. $[Pt(CNC_2H_5)_4][Pt(CN)_4]$, 50600-85-6; $[Pt(CNCH_3)_4][Pt(CN)_4]$, 50600-86-7; $[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$, 50600-88-9.

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Reaction of 1,1′-Bis(diphenylphosphino)ferrocene with Mercuric Halides, Mercuric Cyanide, and Other Lewis Acids

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The reaction of 1,1′-$Fe(cpPPh_2)_2$ with HgX_2 (X = Cl, Br, I, SCN) gives $Fe(cpPPh_2)_2 \cdot nHgX_2$ (n = 1, 2). Infrared, electronic absorption, polarographic, and ^{57}Fe Mossbauer spectroscopic data are presented to show that in every case it is the phosphorus not the iron atom that is bonded to the mercury. The reaction of 1,1′-$Fe(cpPPh_2)_2$ with $Hg(CN)_2$ in the presence of acid gives $[(Fe(cpPPh_2)_2)_2Hg](X)_2$ ($X^- = BF_4^-, PF_6^-$) where physical data show that the dication has a P-Hg interaction. Ruthenocene reacts with SnX_4 (X = Cl, Br) to give compounds with Ru-Sn bonds. The products of the reaction of 1,1′-$Fe(cpPPh_2)_2$ and SnX_4 are described.

Introduction

The mercury-bridged cation $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ is the product of electrochemical oxidation of ruthenocene at a mercury anode.[1] The reaction of mercuric halides with ruthenocene also gives compounds with mercury-ruthenium bonds.[2,3] In the case of ferrocene a red diamagnetic material with the composition $Fe(cp)_2 \cdot 7HgCl_2$ can be isolated.[2] Indications of an Fe-Hg interaction were seen in the infrared spectrum of this red compound.

In this paper we report the results of a study of the interaction of various 1,1′-disubstituted ferrocenes with HgX_2 (X = Cl, Br, I, CN, SCN). Of particular interest is the case where the 1,1′-disubstituted ferrocene is 1,1′-bis(diphenylphosphino)ferrocene, $Fe(cpPPh_2)_2$. This ferrocene was recently prepared by Davison, *et al.*,[4] as a potential bidentate ligand and two very recent reports have shown that it does coordinate to platinum[5] to give $Pt[Fe(cpPPh_2)_2](n\text{-}Bu)_2$ and $Pt[Fe(cpPPh_2)_2]Cl_2$ and to molybdenum[6] to give $Mo(N_2)_2$-

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