Magnetic Circular Dichroism of d^8 Square-Planar Complexes

A. J. McCaffery,[1] P. N. Schatz,[1] and P. J. Stephens[2]

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia, and University of Southern California, Los Angeles, California. *Received April 18, 1968*

Abstract: We have studied the magnetic circular dichroism (MCD) of $PtCl_4^{2-}$, $PdCl_4^{2-}$, $PdBr_4^{2-}$, $AuCl_4^-$, $AuBr_4^-$, and $Pd(NH_3)_4^{2+}$ in solution and K_2PtCl_4 crystal at 4°K over the visible–uv spectral region. Our results strongly suggest that the transition at $\sim$30,000 cm^{-1} in $PtCl_4^{2-}$ is $^1A_{1g} \rightarrow {}^1E_g$ as was suggested previously by Martin and coworkers,[3] and we are able to assign the same transition in several of the other ions studied. We are not able to throw additional light on the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition and thus on the position of the d_{z^2} metal orbital. In the charge-transfer region of the halides, our results support the assignments of the first and second strong bands, respectively, as the ligand-to-metal transitions $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ and $^1A_{1g} \rightarrow {}^1E_u(\sigma)$ except for $PtCl_4^{2-}$. In that case, the first band is overlapped by a transition which could be due to a $5d \rightarrow a_{2u}$ (metal $6p_z$) transition suggested to be in this region by several workers.

The work of Martin, Foss, and coworkers[3] has indicated the potential of Faraday effect studies for the solution of spectroscopic problems in the d^8 square-planar halides. We here report the results of an investigation of the magnetic circular dichroism of the $4d^8$ and $5d^8$ halides (and one tetraammine) over the whole visible–near uv spectral range.

The identification of degenerate states by the study of the dispersion of MCD through absorption bands and the use of the experimental Faraday parameters as a critique of the theoretical description of molecules has recently been extensively demonstrated.[3,4] Having nondegenerate ground states and both degenerate and nondegenerate excited states, the d^8 tetrahalides appear to be eminently suited for study by MCD. The electronic structure of this particular group of compounds has been much discussed in the past, and many attempts have been made to assign the absorption bands observed in solutions and single crystals.

The main features of the dispersion of MCD through absorption bands have been outlined previously.[4,5] To summarize, the magnetic field causes a Zeeman splitting of degenerate ground and excited states. In the case of a degenerate ground state, this leads to the Faraday C term which is temperature dependent and which peaks at the maximum of the corresponding absorption band. When only the excited state is degenerate, we get the Faraday A term which changes sign at the absorption maximum. When both are degenerate, it can be shown that at room temperature and in solutions the C terms usually swamp the A terms. There is a third effect, namely the mixing of states by the magnetic field, and this gives rise to the B term which has the same frequency form as the C term but is not temperature dependent. In general, the B term is present whatever the degeneracies of the states. It is the only term present for transitions with nondegenerate ground and excited states. The relative magnitudes of A and B terms can vary greatly and depend on the individual case.

Experimental Section

Samples of $KAuCl_4 \cdot 2H_2O$, $KAuBr_4 \cdot 2H_2O$, and K_2PtCl_4 were generously supplied by Dr. C. K. Jørgensen, K_2PdCl_4 by Dr. B. G. Anex, and $Pd(NH_3)_4(ClO_4)_2$ by Dr. H. B. Gray. K_2PdBr_4 was obtained from K & K Laboratories, Inc., and was recrystallized before use. We were unable to obtain a sample of K_2PtBr_4 with an absorption spectrum in agreement with that published.[6]

Since most of the absorption and MCD spectra reported here were recorded in solution, some remarks on the nature of the solution species are in order.

Most of the complexes examined here are known to be unstable with respect to solvation under certain conditions. The Pd^{2+} halides seem to be worst in this respect, and much work has been done on them. Radioactive exchange studies[7] show a rapid exchange of labeled halogen with ligand in aqueous solution, and spectrophotometric studies in 1 M[8] and 4 M[9] $HClO_4$ indicate the presence of four-, five-, and six-coordinated species. This latter evidence may not be too relevant however, since oxidation to Pd^{4+} may occur in perchloric acid,[10] but Harris, *et al.*,[11] found a high tendency to hexacoordination in any solvent of moderate donor ability.

In these circumstances it is difficult to be precise about the species present at a given time. However, in the case of $PdCl_4^{2-}$, Anex and Takeuchi[10] have found that a solution of K_2PdCl_4 in 2 M HCl obeys Beer's law and agrees with the single-crystal polarized reflection spectrum, although in other concentrations of acid and in water this is not the case. We find that K_2PdBr_4 in 2 M HBr also obeys Beer's law, and the spectrum agrees with published figures.[6] We have, therefore, assumed the 2 M acid solutions to contain predominantly the PdX_4^{2-} species, and our absorption and MCD results are those obtained in 2 M HCl or HBr.

The gold halides are also known to hydrolyze rapidly in aqueous solution from kinetic[12] and isotopic exchange[13] data. Our spectra were measured in both 1 M KCl or KBr and in 1 M $HClO_4$,

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(1) University of Virginia.

(2) University of Southern California.

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Table I.[a] Summary of Results and Assignments

Complex	Transition frequency, cm^{-1}	ϵ_{max}	Assignment	A[b]	D[c]	A/D
$PtCl_4^{2-}$ in 0.5 M HCl	(18,000)	(5)				
	21,100	16.3				
	25,500	52.6	$^1A_{1g} \rightarrow {}^1A_{2g}$			
	30,300	62.4	$^1A_{1g} \rightarrow {}^1E_g$	−0.093	0.093	−1.0
	(37,600)	(400)				
	(43,400)	(8,500)	$^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$			
	46,200	10,900	5d → 6p[d]			
K_2PtCl_4 crystal (∼4.2°K)	21,300	. . .[e]				
	27,100	. . .[e]	$^1A_{1g} \rightarrow {}^1A_{2g}$			
	30,000	. . .[e]	$^1A_{1g} \rightarrow {}^1E_g$	−0.023	0.024	−0.96
$PdCl_4^{2-}$ in 2 M HCl	(16,200)					
	21,100	152	$^1A_{1g} \rightarrow {}^1E_g$	−0.085	0.288	−0.30
	(30,200)	(540)				
	35,800	10,400	$^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$			
	44,900	28,300	$^1A_{1g} \rightarrow {}^1E_u(\sigma)$	7.27	26.4	0.28
$PdBr_4^{2-}$ in 2 M HBr	19,600	316	$^1A_{1g} \rightarrow {}^1E_g$	−0.056	0.491	−0.11
	(27,000)	(4,000)				
	30,100	11,500	$^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$			
	40,500	30,800	$^1A_{1g} \rightarrow {}^1E_u(\sigma)$	5.40	36.5	0.15
$Pd(NH_3)_4^{2+}$ in H_2O	33,800	200	$^1A_{1g} \rightarrow {}^1E_g$	−0.094	0.344	−0.27
$AuCl_4^-$ in 1 M $HClO_4$	(25,800)	(450)				
	32,000	5,300	$^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$			
	44,500	27,500	$^1A_{1g} \rightarrow {}^1E_u(\sigma)$	6.2	39.1	0.16
$AuBr_4^-$ in 1 M $HClO_4$	(18,000)	(200)				
	(22,100)	(1,200)				
	26,200	4,400	$^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$			
	39,500	36,300	$^1A_{1g} \rightarrow {}^1E_u(\sigma)$	6.1	36.4	0.17

[a] Shoulders are in parentheses. [b] From gaussian fit[4c] in units $D^2\beta$ (D = Debye, β = Bohr magneton). [c] From numerical integration or gaussian fit (if bands overlap) in units of D^2. [d] This assignment is speculative; see text for further discussion. [e] Published ϵ values[16a] used to determine product of concentration and path length for this crystal.

the results being virtually identical in both and the absorption spectra in agreement with published data.[6] $PtCl_4^{2-}$ appears to be much more stable,[14] and the absorption and MCD of this ion were obtained in 0.5 M HCl. In all cases, solutions were made up immediately before running, which meant that solutions were a maximum of 15 min old after completion of the absorption or MCD.

In view of these structural uncertainties, deductions based on the magnitude of the MCD may not be completely reliable due to deviations from square-planar tetrahalide structure in solution, and it is not impossible for A terms to be absent for this reason.

Large single crystals of K_2PtCl_4 were grown from 0.5 M HCl. The complex crystallizes as needles elongated along the c axis. For MCD purposes, light must be propagated down the unique axis of the tetragonal crystal to avoid linear birefringence, and samples suitable for transmission spectroscopy were obtained by grinding down perpendicular to the needle axis until a sufficiently thin section was obtained.

MCD spectra were measured by techniques described in detail elsewhere.[4c] The results together with corresponding absorption spectra obtained on a Cary 14 are displayed in Figures 2–8. $[\theta]_M$ is the molar ellipticity, defined as in natural optical activity, per unit magnetic field in the direction of the light beam. This sign convention is now used by most workers but is opposite to that used in earlier magnetooptical rotation work. With our convention, the Verdet constant of water is negative.

Values of the relevant parameters extracted from the data as described previously[4c] are presented in Table I. We do not list B term values since they are not of quantitative interest for this work. As discussed previously,[4e] the accuracy of our MCD data is determined chiefly by the ratio of peak MCD to maximum absorption. This is fairly favorable for the d → d bands in solution, and the MCD data in such cases should be accurate to about ±10%. The situation is considerably less favorable for the charge-transfer transitions in solution and the d → d transitions in the crystal (which was quite tiny), and in these cases we estimate an accuracy of about ±25%. The gaussian fits of the A terms are quite satisfactory, and even in the most unfavorable case A/D values should be reliable within a factor of 2 when all uncertainties (including the assumption of a gaussian model for band shape) are taken into account.

Discussion

The relevant molecular orbital energy levels of square-planar metal halide complexes are shown diagrammatically in Figure 1. Possible transitions can be divided into two groups: (1) excitations between the d orbitals and (2) others, comprising ligand-to-metal, metal-to-ligand, intrametal, or intraligand transitions. The former are all parity forbidden and therefore weak; the latter can be both weak and strong.

d → d Bands. Weak absorptions have been observed in the room-temperature solution spectra of the accessible square-planar halides,[6] in the room-temperature crystal spectra of $PtCl_4^{2-}$ and $PdCl_4^{2-}$,[15,16a] in the solution spectrum of $AuCl_4^-$ at 77°K,[17] and in the single-crystal spectrum of K_2PtCl_4 at 15°K.[16] These have been attributed to d → d transitions. In the absence of spin–orbit coupling the three d → d excitations give rise to $^{1,3}A_{2g}$, $^{1,3}B_{1g}$, and $^{1,3}E_g$ excited states; inclusion of spin–orbit coupling splits and scrambles these states in proportion to the magnitude of the coupling. Several different spectral assignments have been made depending on the d-orbital order adopted and on whether spin–orbit coupling was taken into account, and these have been summarized by Day, *et al.*,[15] and Martin, *et al.*[16a] The ion most extensively studied is $PtCl_4^{2-}$. It is salutary to notice that, despite measurement of the 15°K polarized absorption spectrum[16] and a "complete" d-electron calculation,[18a] the assignment of the $PtCl_4^{2-}$ spectrum remains un-

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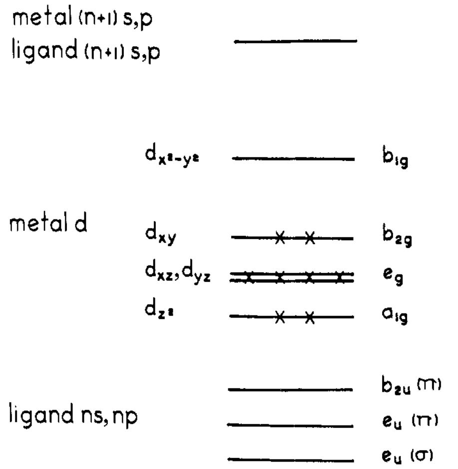

Figure 1. Schematic molecular orbital energy level diagram for a square-planar d^8 metal halide complex. Crosses denote electrons in the ground state. Only those ligand orbitals are shown which can give rise to allowed ligand-to-metal transitions.

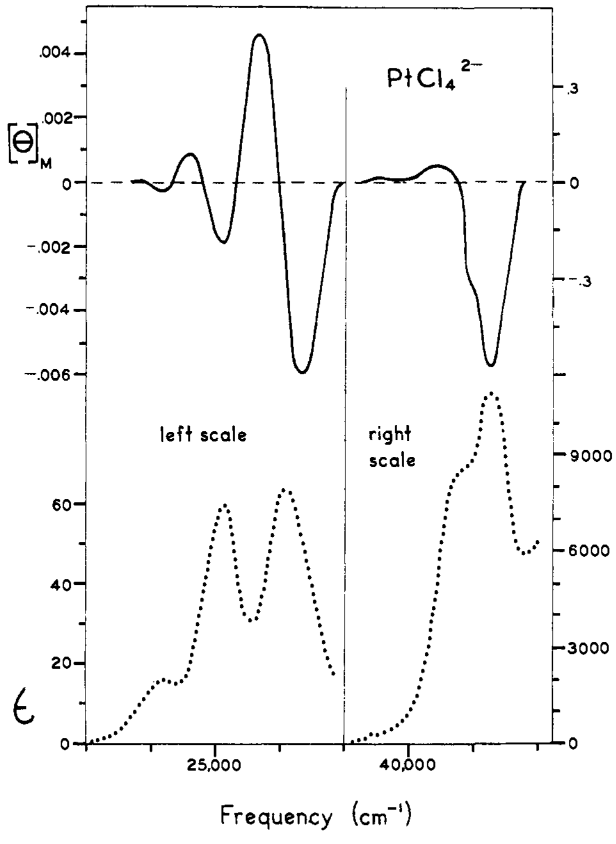

Figure 2. Absorption spectrum and MCD of $PtCl_4^{2-}$ in 0.5 *M* HCl. $[\theta]_M$ is the molar ellipticity (defined as in natural optical activity in degrees deciliter decimeter⁻¹ mole⁻¹) per gauss in the direction of the light beam. ε is the molar extinction coefficient.

settled owing to the magnitude of the spin–orbit coupling and the large number of unknown parameters. This shows that it is risky to attempt detailed assignments using solution data alone.

The solution MCD of $PtCl_4^{2-}$ (Figure 2) shows an *A*-type term at 30,000 cm⁻¹, as first observed by Martin, *et al.*,[3] and this is closely reproduced in the crystal MCD at 4°K (Figure 3). This is consistent with the assignment of this band to the degenerate $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_5(^1E_g)$ transition and hence with the proposals of Chatt, Gamlen, and Orgel,[19] Gray and Ballhausen,[18c] and Martin, *et al.*,[18a] but not Fenske, Martin, and Ruedenberg.[18b] However, it does not eliminate the possibility that this band also contains the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_3(^1B_{1g})$ transition and hence does not distinguish the two assignments of Martin, *et al.*[18a] The change in sign could also conceivably arise from two overlapping bands with *B* terms of opposite sign. However, this does not seem very likely in this case; in particular, the overlapping of Γ_3 and Γ_5 states, suggested in assignment *B* of Martin, *et al.*, should not give a large term of this kind in the crystal MCD as Γ_3 and Γ_5 are not mixed by a field along the fourfold molecular axis. It should be noted that the reduction in $[\theta]_M$ and ε for the crystal at low temperature is just the behavior one would expect for a vibronically allowed (d → d) transition. We see from Table I, however, that the *ratio A/D* agrees well between solution and crystal.

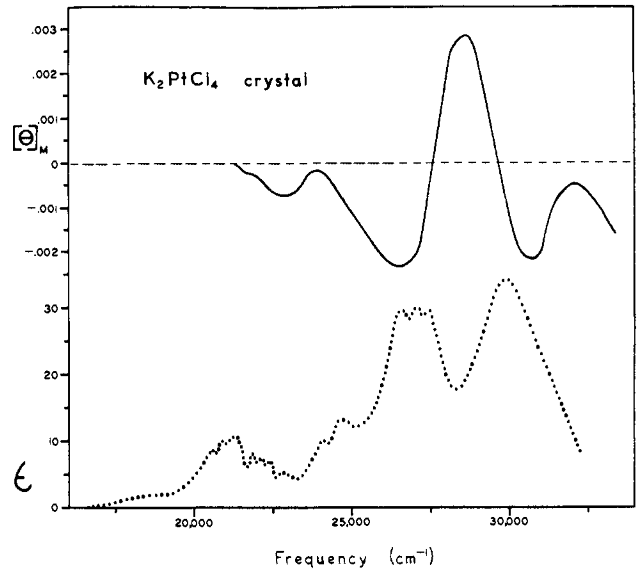

Figure 3. Absorption spectrum and MCD of crystalline K_2PtCl_4 at ~4.2°K. ε values from ref 16a were used to calculate the product of concentration and path length for this crystal. Units are as in Figure 2.

The $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_2(^1A_{2g})$ assignment for the 25,500-cm⁻¹ transition (27,100 cm⁻¹ in the crystal) is well established by the polarization properties in the crystal and by the acquired optical activity in (−)-2,3-butanediol.[20] The MCD is consistent with assignment to a nondegenerate excited state since only a *B* term is observed. The nature of the shoulder at 37,600 cm⁻¹ in solution is not clarified; only a small *B* term is observed, and it seems likely to be a nondegenerate transition. The solution MCD changes sign in places at lower energies; however, the zeros nowhere coincide with clearly defined absorption maxima and the MCD probably just results from overlapping *B* terms.

The MCD of $PdCl_4^{2-}$ (Figure 4) likewise shows an apparent *A* term at 21,100 cm⁻¹. In the room-tem-

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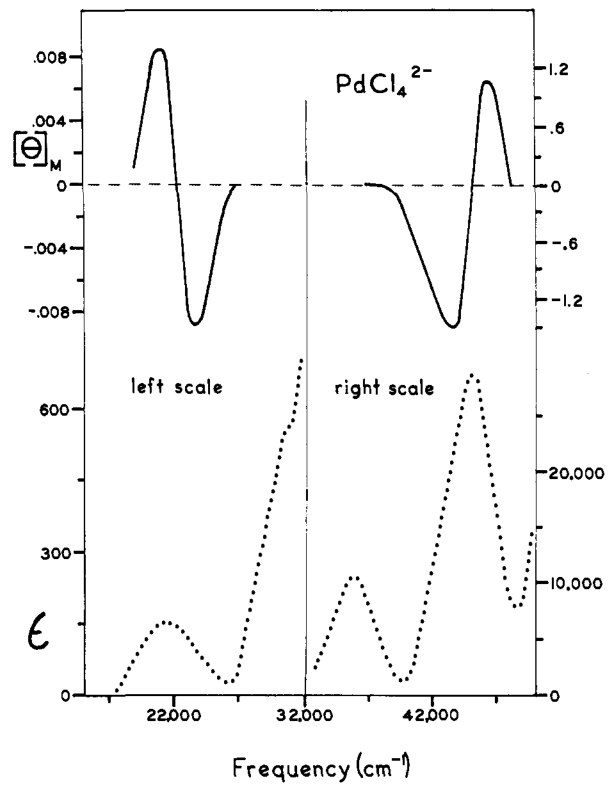

Figure 4. Absorption spectrum and MCD of $PdCl_4^{2-}$ in 2 *M* HCl. Units are as in Figure 2.

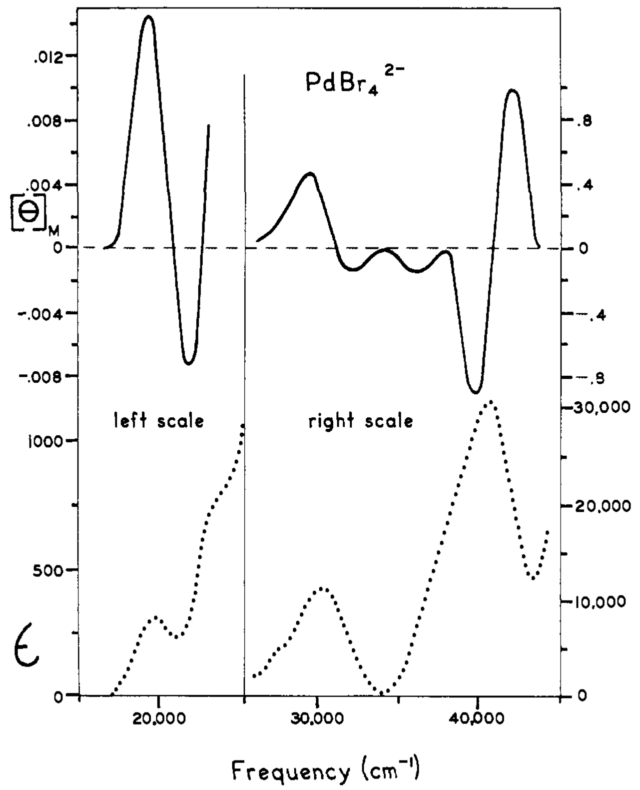

Figure 5. Absorption spectrum and MCD of $PdBr_4^{2-}$ in 2 *M* HBr. Units are as in Figure 2.

perature crystal spectra of K_2PtCl_4 and K_2PdCl_4, the 21,100-cm^{-1} band in the latter is very similar in appearance and polarization to the 30,000-cm^{-1} band of the former. It seems very reasonable to make the same assignment, therefore, in agreement again with Chatt, *et al.*,[19] Ballhausen and Gray,[18c] and Basch and Gray,[18d] but not Fenske, Martin, and Ruedenberg.[18b] The same assignment also applies to the 19,600- and 33,800-cm^{-1} bands in $PdBr_4^{2-}$ (Figure 5) and $Pd(NH_3)_4^{2+}$ (Figure 6), respectively.

High-Intensity bands. The high-intensity absorptions are generally referred to as charge-transfer bands, although they could also be due to transitions from the d shell to a mainly metal $(n + 1)$p orbital or to essentially intraligand transitions. Most assignments have placed them in the ligand-to-metal charge-transfer category, and this is supported by the shifts of the intense bands as a function of metal oxidation number.[6] Three allowed ligand-to-metal charge-transfer transitions are expected, namely $b_{2u}(\pi)$, $e_u(\pi)$, and $e_u(\sigma)$ $\rightarrow d_{x^2-y^2}$, giving the excited singlet states $^1A_{2u}$, $^1E_u{}^{(1)}$, and $^1E_u{}^{(2)}$, respectively. The Pd^{2+} and Au^{3+} halides (Figures 4, 5, 7, 8) each show two strong bands in the near-uv. Gray and Ballhausen[18c] originally assigned the longer and shorter wavelength bands to $^1A_{2u}$ and $^1E_u{}^{(1)}$, respectively. However, Jørgensen[6] suggested the first band to be $^1A_{2u} + {}^1E_u{}^{(1)}$ and the higher energy transition $^1E_u{}^{(2)}$, on the grounds that the intensity of the latter is more consistent with a $\sigma \rightarrow d_{x^2-y^2}$ transition than with $\pi \rightarrow d_{x^2-y^2}$. Basch and Gray[18d] and Gray[18e] later adopted Jørgensen's assignment on the basis of MO calculations. Anex and Takeuchi[10] have recently provided the first experimental support for this assignment by measuring the polarized reflection spectrum of K_2PdCl_4. This shows both bands to be strongly in-plane polarized and hence to involve predominantly ^1E_u excited states. The moderately intense band at 46,000 cm^{-1} in $PtCl_4^{2-}$ has similarly been assigned as $^1A_{2u}$ or $^1A_{2u} + {}^1E_u{}^{(1)}$. However, recent MO calculations by Cotton and Harris[21] on $PtCl_4^{2-}$ predict the lowest allowed transition to be 5d $\rightarrow$ a_{2u}(metal 6p) in character. Further, Anex and Takeuchi[10] have shown that this band is predominantly out-of-plane

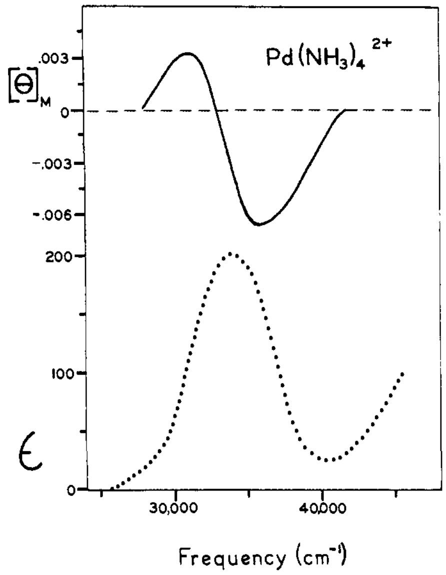

Figure 6. Absorption spectrum and MCD of $Pd(NH_3)_4^{2+}$ in water. Units are as in Figure 2.

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[21] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 6, 369 (1967).

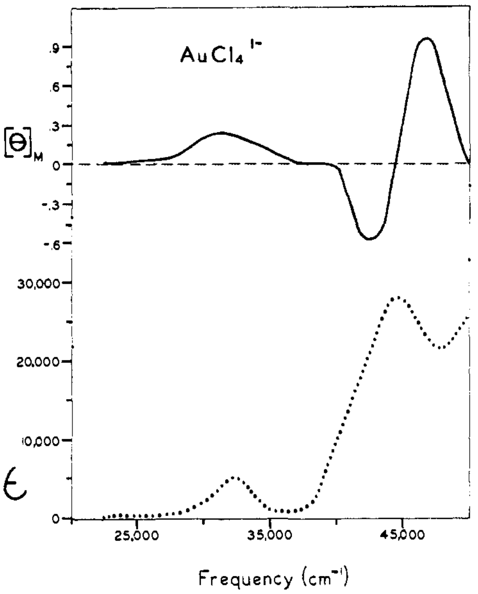


Figure 7. Absorption spectrum and MCD of $AuCl_4^-$ in 1 *M* $HClO_4$. Units are as in Figure 2.

polarized and have also suggested the 5d → $6p_z$ assignment. It thus appears likely that in $PtCl_4^{2-}$ the transitions out of the filled d shells are as low in energy as those into the empty $d_{x^2-y^2}$ orbital.

The MCD of the Pd^{2+} and Au^{3+} halides are very similar, suggesting common assignments of their absorption spectra. $PdBr_4^{2-}$ appears to show a small *A* term in the lower energy band, and this gives support to the assignment of this band as the composite $^1A_{2u}$ + $^1E_u^{(1)}$. Apparently in the other Pd^{2+} and Au^{3+} ions the *A* term is too small to be detected under the *B* terms. The unambiguous *A* terms under the strong bands of all four of these halides are in accord with an assignment to a ^1E_u state. Note that they are opposite in sign to the *A* term under the weaker band in $PdBr_4^{2-}$. Assignment to metal-to-ligand (or other) transitions is not excluded by the qualitative MCD features. However, quantitative considerations support the ligand-to-metal scheme. In the latter, degenerate transitions arise from excitation from a degenerate, mainly ligand orbital to the nondegenerate $d_{x^2-y^2}$ orbital. The *A* term then depends on the angular momentum of the ligand orbital alone. Conversely, for metal-to-ligand transitions, at least some of the degenerate states are due to transitions from the metal e_g orbital to a nondegenerate empty orbital and thus possess the angular momentum of the d orbital. Simple considerations of a kind illustrated in earlier papers[4] show that the angular momenta of the $e_u(\pi)$ and $e_u(\sigma)$ ligand MO's in a square-planar complex are expected to be much smaller than that of a d orbital and, in fact, arise only through σ–π mixing. The magnetic moment (μ) of the $^1E_u^{(2)}$ states of $AuCl_4^-$, $AuBr_4^-$, $PdCl_4^{2-}$, and $PdBr_4^{2-}$ can be evaluated from their *A* terms in the manner described previously.[4] One finds that $|A/D| = |\mu/2|$. We thus obtain $|\mu|$ values of 0.32, 0.34, 0.55, and 0.30, respectively (in Bohr magnetons). These values are considerably smaller than the magnetic moment of a d orbital supporting the ligand-to-metal assignment. Also, empirical evidence is provided by comparison with the MCD of $Ni(CN)_4^{2-}$.[4g] Here $[\theta]_{M,max}/\epsilon_{max}$ for the *A* term observed is an order of magnitude larger, in accord with its assignment to a metal-to-ligand transition. These deductions could be invalidated if, in fact, the species in solution are not the MX_4^{n-} ions; however, it seems unlikely that all the halides studied decomposed to the same extent.

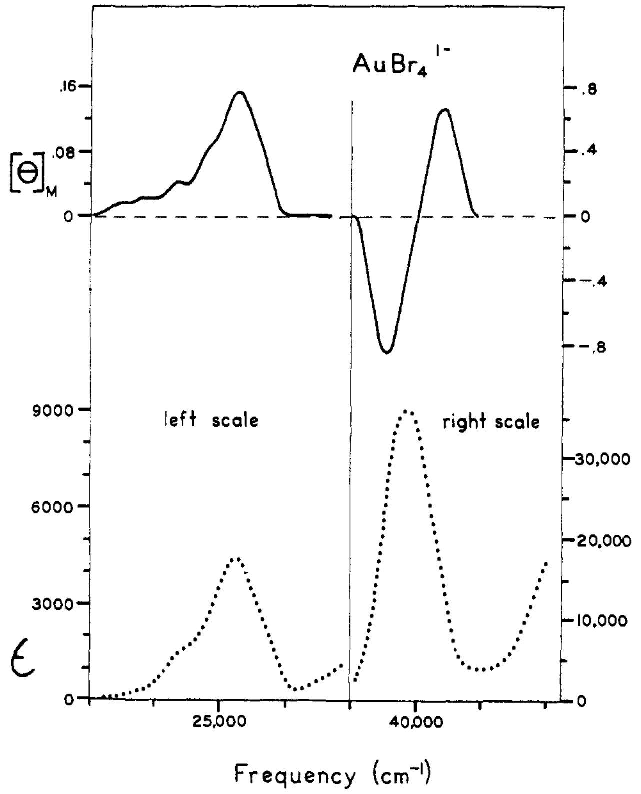


Figure 8. Absorption spectrum and MCD of $AuBr_4^-$ in 1 *M* $HClO_4$. Units are as in Figure 2.

The MCD of the 46,000-cm^{-1} band in $PtCl_4^{2-}$ is quite different in over-all qualitative appearance from that of the Pd^{2+} and Au^{3+} ions and, like the polarized reflection spectrum, suggests a different assignment for this band. The lower energy component, however, appears to exhibit an *A* term of the same sign as observed in the first $PdBr_4^{2-}$ band. It seems reasonable therefore to assign this to the $^1E_u^{(1)}$ transition and the dominant, higher energy band to the 5d → a_{2u}(metal $6p_z$) transition suggested by Cotton and Harris[21] and Anex and Takeuchi[10] as discussed above.

Conclusions

This MCD study has clarified a number of points regarding the spectroscopy of d^8 square-planar complexes. We have demonstrated that the absorption at ~30,300 cm^{-1} in $PtCl_4^{2-}$ is $^1A_{1g} \rightarrow {}^1E_g$ (xz, $yz \rightarrow x^2 - y^2$) as pointed out in an earlier MCD study by Martin, *et al.*,[3] and we have further confirmed this by a study of crystalline K_2PtCl_4 at ~4°K. In a similar manner, we have shown that the same assignment applies for the bands at 21,100, 19,600, and 33,800 cm^{-1} in $PdCl_4^{2-}$, $PdBr_4^{2-}$, and $Pd(NH_3)_4^{2+}$, respectively. We did not identify the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition and thus cannot say anything new about the position of the metal d_{z^2} orbital. Proceeding to higher energies, our

MCD results on the Pd and Au halides support Jørgensen's[6] assignment of the two intense bands as $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ and $^1A_{1g} \rightarrow {}^1E_u(\sigma)$. For $PtCl_4^{2-}$, we identify the shoulder at 43,400 cm^{-1} as the $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ transition, but the main band at 46,200 cm^{-1} appears to be of quite different character and may well be the 5d → a_{2u}(metal $6p_z$) transition suggested by Cotton and Harris[21] and Anex and Takeuchi.[10]

Acknowledgments. We are deeply indebted to Drs. Jørgensen, Anex, and Gray for supplying us with chemical samples and to Drs. Anex and Takeuchi for permission to quote their reflection results prior to publication. We are also indebted to Mrs. K. Victor for help in the measurement of the absorption spectra. This work was supported in part by a grant from the National Science Foundation.

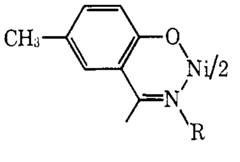
Diastereoisomeric Four-Coordinate Complexes. VI.[1] Paramagnetic Nickel(II) Complexes with Four Asymmetric Ligand Centers

R. E. Ernst,[2] M. J. O'Connor, and R. H. Holm[3]

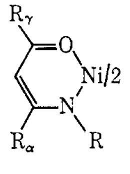
Contribution from the Departments of Chemistry, University of Wisconsin, Madison, Wisconsin, and Massachusetts Institute of Technology, Cambridge, Massachusetts. *Received April 18, 1968*

Abstract: A series of bis-chelate nickel(II) complexes containing four asymmetric ligand centers occurring as two inequivalent pairs has been synthesized, and their proton resonance spectra have been investigated in order to determine to what extent the contact shift method can detect all possible diastereoisomers. The complexes examined are of the bis(salicylaldimine) type having the general formulation Ni(X-R-sal)$_2$, in which X = 3*s*Bu, 5Me and R = CH_3CHCH_2Ph (Amp), CH_3CHPh (PhEt), and *sec*-Bu (= *s*Bu). All complexes are shown to exist in the dynamic planar ⇌ tetrahedral equilibrium in chloroform solution. It is demonstrated that, apart from the absolute configuration at the metal in the tetrahedral form, six pmr-distinguishable diastereoisomers are possible for complexes prepared from racemic ligand components. Signals corresponding to the six isomers were observed in the pmr spectra of the three groups of complexes. A general method of signal assignments for the Ni(X-R-sal)$_2$ isomers is described and applied to Ni(3*s*Bu-Amp-sal)$_2$, resulting in unequivocal assignment of certain signals to the six possible isomers. The marked sensitivity of the pmr method in detecting diastereoisomers arises from the contact interaction and the presence of the structural equilibrium, for which the ΔF value of each diastereoisomer is measurably different. These values are considered to differ principally because of inequalities in the free energies of the paramagnetic, tetrahedral forms which in turn are produced by the various sets of intramolecular (R–R, R–X) interactions. Intrinsic differences in electron-nuclear coupling constants are shown to be unimportant in producing the primary chemical shift separation between R-active and R-*meso* sets of isomers with R = Amp. The sets of thermodynamic parameters (ΔF, ΔH, ΔS) describing the planar–tetrahedral structural change of the six diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ have been derived from the temperature dependence of the contact shifts of each isomer.

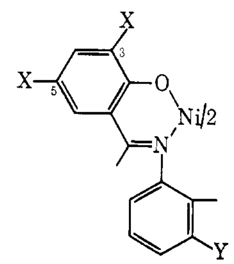
Our recent investigations of diastereoisomeric four-coordinate metal(II) complexes[1,4–6] have been undertaken with the purpose of detecting and identifying all possible isomers and determining the stabilities of the planar and tetrahedral stereoisomers and the enantiomeric configurations of the latter. This work has been principally concerned with nickel(II) complexes[1,4,5] because of the simultaneous population of both planar and tetrahedral configurations in many cases and the presence of large proton contact shifts from the tetrahedral isomers which greatly amplify the intrinsic chemical shift differences between corresponding nuclei in different diastereoisomers. Three groups of complexes have been examined in detail by proton resonance: the bis(salicylaldimines) **1**,[4,5] the bis(β-ketoamines) **2**,[5] and the 2,2′-bis(salicylideneamino)biphenyls **3**.[1]



1



2



3

The tetrahedral forms of **1**, **2**, and **3** are enantiomeric, giving rise to the Δ and Λ absolute configurations, which have been defined previously[5] to possess right-handed and left-handed chirality, respectively, with reference to the C_2 axis of the molecule. The Δ and Λ configurations of **3** are formed with complete stereospecificity

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[1] Part V: M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

[2] National Institutes of Health Predoctoral Fellow.

[3] Author to whom correspondence should be addressed at Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

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