Inorg. Chem. **1993,** *32,* 3909-3914

Electronic Structure and Spectra for Square Complexes Containing Sulfur-Donor Ligands: $M(dto)_2^{2+}$ (M = Pt(II), Pd(II); dto = 3,6-Dithiaoctane), $M(SCN)_4^{2-}$ (M = Pt(II), Pd(II)), and $M(Et\text{-}Xan)_2$ (M = Pt(II), Pd(II), Ni(II); $Et\text{-}Xan^- = C_2H_5OCS_2^-$)

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Received March 17, 1993

Electronic absorption and magnetic circular dichroism (MCD) spectra in the UV-visible region are reported for acetonitrile solutions of $[M(dto)_2](ClO_4)_2$, dto = 3,6-dithiaoctane, M = Pt(II) and Pd(II); $[(n\text{-}C_4H_9)_4N]_2[M(SCN)_4]$, M = Pt(II) and Pd(II); and $M(Et\text{-}Xan)_2$, $Et\text{-}Xan^-$ = ethyl xanthate, M = Pt(II), Pd(II), and Ni(II). The intense bands and the MCD B terms observed for the Pd(II) and Ni(II) complexes are generally assigned to ligand to metal charge transfer (LMCT) from orbitals of the S donor to the empty metal $d\sigma^*$ orbital ($nd_{x^2-y^2}$). However, the MCD in the region 3.8–5.0 μm^{-1} for the Pt(II) complexes is stronger and differs in pattern from the MCD associated with the LMCT bands and is attributed to the presence of Pt(II) localized $5d \rightarrow 6p_z$ excitations. The most intense LMCT bands, which follow the energetic trend Pt(II) > Pd(II) > Ni(II), are ascribed to $S\sigma \rightarrow d\sigma^*$. Some internal ligand transitions are also identified in the spectra of the $Et\text{-}Xan^-$ complexes. The donor behavior of the dto, SCN^-, and $Et\text{-}Xan^-$ ligands in the square MS_4 complexes is discussed.

Introduction

Over the last three decades the electronic structure and spectra for square planar complexes for metal ions of d^8 electronic configuration have been extensively investigated for halide, CN^-, N-donor ligands, P-donor ligands, and chelating S-donor dithiolato ligands.[1-4] Patterns of energy levels and excited states have been developed which now seem to be accepted. However, apart from the dithiolato complexes,[4] there have been few detailed studies of square complexes with other types of S-donor ligands. This is perhaps surprising in view of the variety of stable S-donor complexes known for Pd(II) and Pt(II). Electronic spectra for some of these complexes have been interpreted by analogy to halide complexes with the reasoning that both X^- and S-donor ligands possess lone pairs and are capable of both σ and π donation to the metal ion. The intense bands observed in the spectra of S-donor complexes have typically been ascribed to ligand to metal charge transfer (LMCT), by analogy to intense LMCT bands observed for halo complexes, or otherwise to internal ligand transitions.[1] The study of S-donor complexes as examples of LMCT was of natural interest in our continuing study of the electronic structure and spectra of square planar complexes,[2] and we report here absorption and magnetic circular dichroism (MCD) spectra in acetonitrile solution for some MS_4 complexes with three different types of S-donor ligands: 3,6-dithiaoctane, $C_2H_5S(CH_2)_2SC_2H_5$ (dto), thiocyanate-*S*, SCN^-, and ethyl xanthate, $C_2H_5OCS_2^-$ ($Et\text{-}Xan^-$). The complexes investigated included $[M(dto)_2](ClO_4)_2$, M = Pt(II) and Pd(II); $[(n\text{-}C_4H_9)_4N]_2[M(SCN)_4]$, M = Pt(II) and Pd(II); and $M(Et\text{-}Xan)_2$, M = Pt(II), Pd(II), and Ni(II). Each of these complexes is presumed to have MS_4 square planar coordination about the metal ion in solution. X-ray crystal structure studies[5,6] indicate the SCN^- complexes are S-bonded and have MSC angles of 104–109°. A structural study[7] also confirms that the $Ni(Et\text{-}Xan)_2$ complex is planar, as are the related aryl xanthato complexes $Ni(4\text{-}t\text{-}BuC_6H_4\text{-}Xan)_2$ and $Pd(2,4,6\text{-}Me_3C_6H_2\text{-}Xan)_2$.[8] There do not seem to be any crystal structures for the dto complexes, but there is little reason to expect a departure from a planar MS_4 arrangement. Polarized single-crystal absorption spectra have been reported[9] for $K_2[M(SCN)_4]$, M = Pt(II) and Pd(II), but this study focused on the weak low-energy ligand field (LF) transitions. The focus of the present study is on the intense bands observed at higher energy.

Experimental Section

Preparation of Compounds. The complexes were prepared from aqueous solutions of $K_2[MCl_4]$, M = Pd(II) and Pt(II), or $NiCl_2 \cdot 6H_2O$. The dto complexes were prepared by adding a 2–4-fold excess of the ligand (Pfaltz and Bauer, Inc.) to an aqueous solution of the $K_2[MCl_4]$ starting material. After heating of the resulting solutions for a time (3 h for Pt or 1 h for Pd), the solutions were concentrated under reduced pressure and the PF_6^- or ClO_4^- salts were precipitated by adding concentrated aqueous solutions of either NH_4PF_6 or NH_4ClO_4. The electronic spectra of the two salts in acetonitrile solution were virtually identical; only the ClO_4^- salts (*Warning: perchlorate hazard!*) were used for the extensive spectral studies of this work. The SCN^- complexes were prepared similarly by treating aqueous solutions of $K_2[MCl_4]$ with a 2–4-fold excess of aqueous KSCN. The $(n\text{-}C_4H_9)_4N^+$ salts were precipitated by adding a concentrated aqueous solution of $(n\text{-}C_4H_9)_4NCl$. Finally the $Et\text{-}Xan^-$ complexes were prepared according to a literature procedure.[10] The product complexes precipitated readily from aqueous solutions of the starting materials upon addition of aqueous K[Et-Xan]. The elemental analysis for each compound was satisfactory.

Spectral Measurements. Solution absorption spectra were checked for Beer's law compliance and were found to obey the relation in acetonitrile to within experimental error in the concentration range of 10^{-3}–10^{-5} M.

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(1) See for example: Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1984; pp 245, 339–354, and 534–553 and references cited therein.

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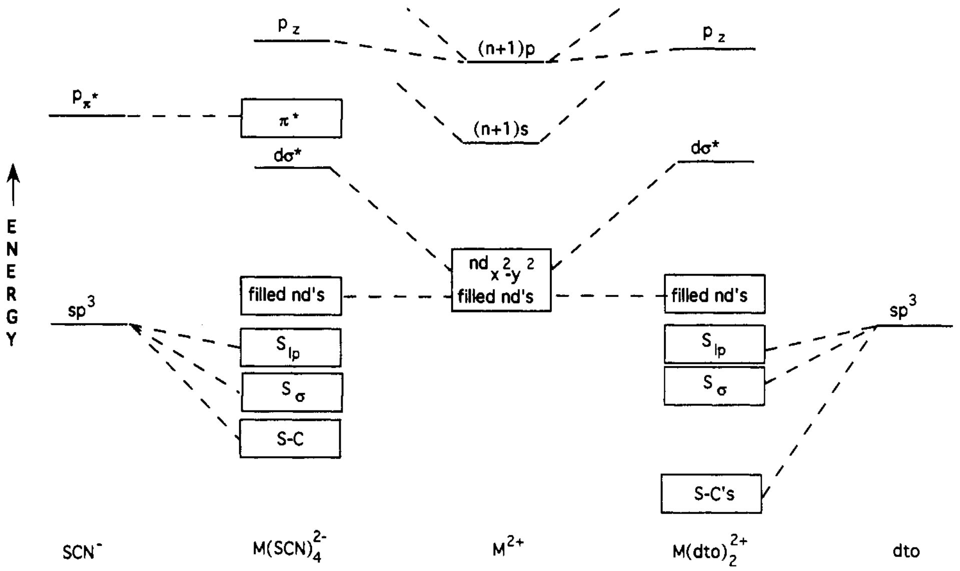

Figure 1. Schematic molecular orbital energy levels for square planar dto (right side) and SCN$^-$ (left side) complexes. Only the ligand S donor orbitals are shown.

The solutions were prepared fresh just before measurements were made and were protected from light. There was no evidence of spectral changes due to solvolysis or photodecomposition during the time required for the spectral measurements (typically 0.5–1 h). Spectra were also obtained for the free uncomplexed ligands in acetonitrile. Absorption spectra were determined by means of a Cary 1501 spectrophotometer. Absorption and MCD spectra were determined simultaneously and synchronously along the same light path by means of a spectrometer described earlier.[11] The magnetic field was provided by a 7.0-T superconducting magnet system (Oxford Instruments SM2-7, which was fitted with a room-temperature bore tube). All spectral measurements were corrected for solvent blank.

Results and Discussion

Molecular Orbitals and Energy Levels. The solution structures of the complexes investigated are not known for certain, but they are all assumed to possess square (D_{4h}) MS$_4$ local coordination about the metal ion. Their full molecular symmetry is certainly lower, but the local symmetry may be used to advantage as a starting point in discussing the MO energy levels for each type of complex. Each S-donor of the dto chelating thio ether ligand presents a lone pair to the metal for σ bonding that is approximately sp^3 hybridized. The nonbonding lone pair is also presumed to reside in an sp^3 hybrid orbital localized mainly on the sulfur donor. This nonbonding pair may be visualized as having a π component and thus some capacity to π bond to the metal, but it is considered unlikely that π bonding will be very extensive due to the orientation of the nonbonding orbital. The dto ligand is probably best viewed as a σ only ligand. The S-bonded SCN$^-$ ligand is bound to the metal ions in an angular fashion with M–S–C angles (104–109° in crystals) that depart significantly from linearity. Therefore, a reasonable model for the S-donor in SCN$^-$ is that of a sp^3-hybridized sulfur with one σ-pair involved in bonding to the metal and two other pairs in hybrid orbitals oriented away from the metal ion. As for the dto ligand the π-donating ability of SCN$^-$ is not expected to be very large. In contrast, the S donors of the Et-Xan$^-$ ligand present a conjugated π system to the metal center in addition to the sp^2 lone pairs used for σ bonding. Figures 1 and 2 present qualitative MO energy level schemes consistent with the features of the S-donor ligands; these schemes will be useful in visualizing the various types of electronic excitations possible for the three kinds of complexes. It should be noted that the metal ions of interest all have nd^8 electron configurations, and therefore the highest occupied orbitals in Figures 1 and 2 are labeled "filled nd's"; the empty dσ* orbital is mainly the metal nd$_{x^2-y^2}$ orbital. In addition it should be noted that a high energy orbital labeled p$_z$ is shown in the figures. This orbital is expected to be of importance for Pt complexes. Consideration of atomic orbital energies show that the 6p orbital of Pt is low enough compared to the 5d orbitals that it should be considered as a possible empty metal orbital accessible by electronic excitations in the UV region. The 5p orbital of Pd, on the other hand, is considerably higher in energy compared to the 4d orbitals and it is unlikely to be involved in excitations possible in the energy range of this study.

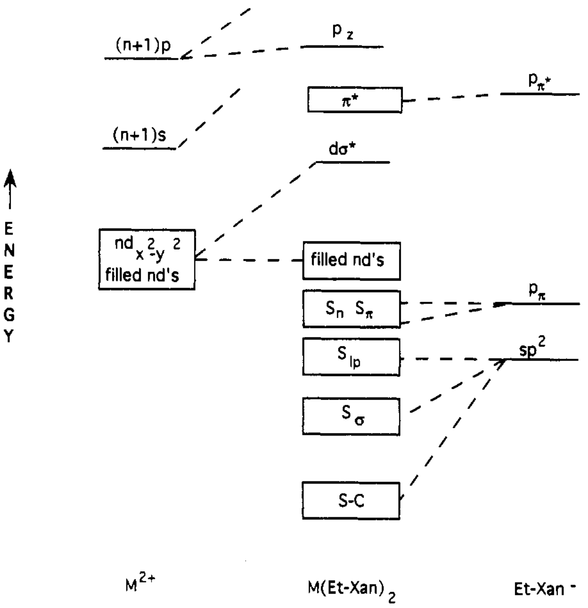

Figure 2. Schematic molecular orbital energy levels for square planar Et-Xan$^-$ complexes. Only the Et-Xan$^-$ S donor orbitals are shown.

Experimental Spectra. Absorption and MCD spectra for acetonitrile solutions are presented in Figures 3–5, while quantitative spectral data are collected in Table I. Table I also includes data for acetonitrile solutions of the free uncomplexed ligands, dto, KSCN, and K[Et-Xan], for comparison purposes. In general the MCD spectra show more spectral detail than the absorption spectra and are better resolved in many cases. The low molecular symmetry of the complexes precludes the observation of genuine MCD A terms resulting from degenerate excited states.[12]

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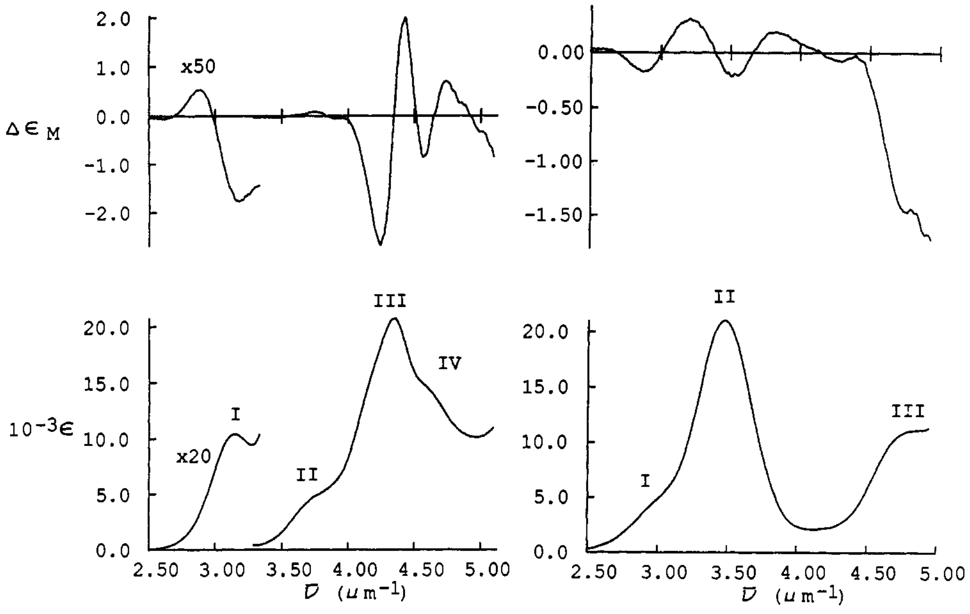

Figure 3. Electronic absorption (lower curves) and MCD (upper curves) spectra for $[Pt(dto)_2](ClO_4)_2$ (left-hand side) and $[Pd(dto)_2](ClO_4)_2$ (right-hand side) in acetonitrile. The units for ϵ and ϵ_M are (M cm)$^{-1}$ and (M cm T)$^{-1}$, respectively.

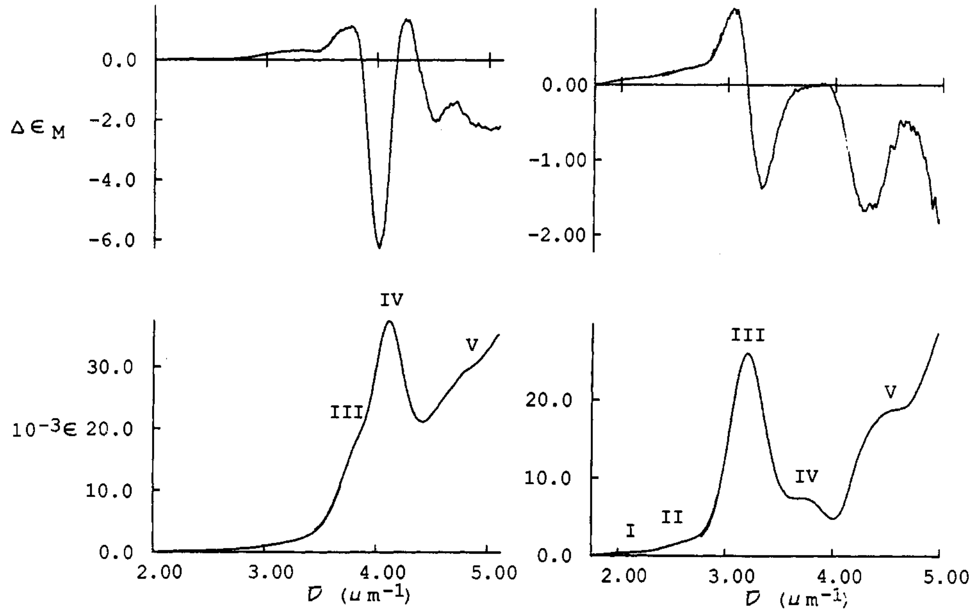

Figure 4. Electronic absorption (lower curves) and MCD (upper curves) for $[(n\text{-}C_4H_9)_4N]_2[Pt(SCN)_4]$ (left-hand side) and $[(n\text{-}C_4H_9)_4N]_2[Pd(SCN)_4]$ (right-hand side) in acetonitrile. Units are as in Figure 3.

However in several cases the MCD gives the appearance of A terms (a positive A term for band III for $Pt(dto)_2^{2+}$ and a negative A term for band III for $Pd(SCN)_4^{2-}$, as examples). These "A" terms (noted in Table I) are formally pseudo-A terms which result from B terms of opposite sign associated with a pair of very close lying states, states which would correlate with an E_u state in D_{4h} symmetry. The observation of such pseudo-A terms can be offered as evidence that the MS_4 coordination in these complexes does not deviate greatly from the local D_{4h} symmetry imposed by the S donors alone.

Spectral Interpretation. The lowest energy absorptions for the complexes studied here are weak, broad bands which in many cases are poorly resolved. These absorptions are ascribed to LF transitions from the filled *n*d's to dσ^*. The MCD in the region of these absorptions is also broad and generally uninformative. Therefore few attempts will be made to give a detailed assignment for these weak absorptions beyond attributing them to LF transitions. As noted in the Introduction the focus of this study is on the more intense bands found at higher energy. The interpretation of these bands will be discussed for each type of complex in the following sections.

dto Complexes (Figure 3). The most intense absorption bands in the spectra (band III for the Pt(II) complex and band II for the Pd(II) complex) appear remarkably similar, but the MCD associated with them is quite different. A strong positive A term is observed for band III of the Pt(II) complex, but a more unsymmetrical and weaker negative A term is seen for band II of the Pd(II) complex. This difference in the MCD is a signal that the two transitions differ in origin, despite the similarity of their absorption. On the basis of the atomic orbital energy differences, band III for the Pt(II) complex is assigned to the Pt localized $5d_{xz}$, $5d_{yz}$ → $6p_z$ transition. The E_u excited state of singlet parentage (D_{4h} approximation) associated with this transition is predicted to have a strong positive A term in the MCD; such transitions with strong positive A terms have been observed for Pt(II) halide, CN$^-$, N-donor, and P-donor complexes.[2] In contrast the 4d → 5p transitions for Pd(II) are expected to be too high in energy to be observed. Therefore band II for the Pd(II) complex is assigned to Sσ → dσ^* LMCT. The high intensity of the transition and a lower energy compared with an analogous transition for Pt(II) are consistent with this assignment. (The Sσ → dσ^* band for the Pt(II) complex may be obscured

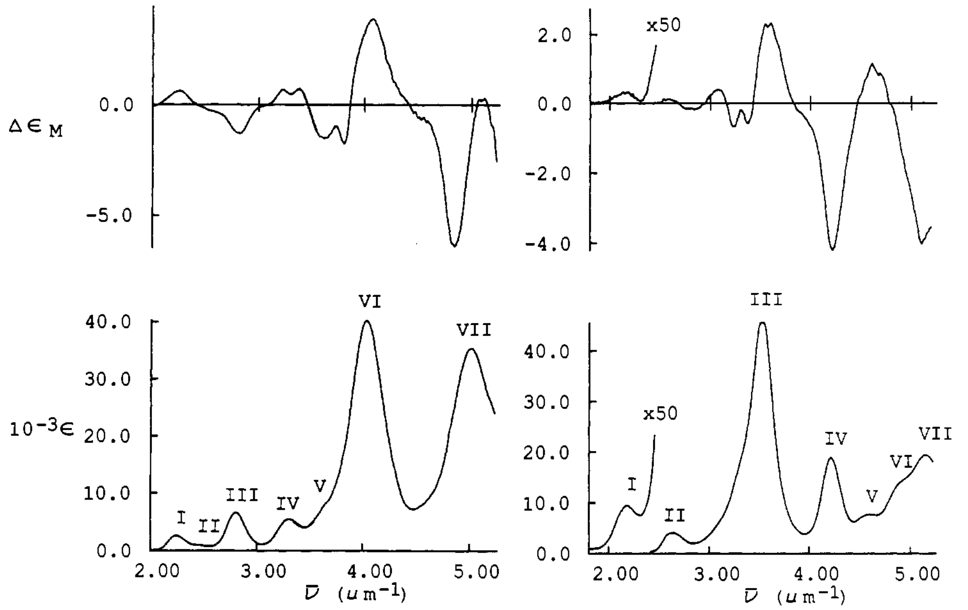

Figure 5. Electronic absorption (lower curves) and MCD (upper curves) for Pt(Et-Xan)$_2$ (left-hand side) and Pd(Et-Xan)$_2$ (right-hand side) in acetonitrile. Units are as in Figure 3.

by the 5d → 6p band III, or it may be at higher energies beyond the range of the present measurements.) Further, it can be shown from ligand–ligand overlap considerations that the two-centered integrals necessary to predict the MCD A term sign for the Sσ → dσ^* band lead to the expectation of a negative term if e_u Sσ and b_{1g} dσ^* symmetries are assumed (again reasonable assumptions in the D_{4h} approximation; see ref 12 for details).

Band II for the Pt(II) complex and band I for the Pd(II) complex also have a similar appearance in the absorption spectra, but their MCD are notably different. The very weak negative A term for band II of the Pt(II) complex is interpreted as resulting from the superposition of two d → p transitions with a near cancellation of the MCD. The E_u spin-orbit states from ^3E_u (5d_{xz}, 5d_{yz} → 6p_z) and $^3B_{1u}$ (5d_{xy} → 6p_z) are predicted to have A terms of opposite sign.[2] Strong spin–orbit coupling on the Pt ($\zeta_{5d} \sim 0.35\ \mu m^{-1}$) allows transitions to these states to gain significant intensity even though they are of triplet parentage. Energetically these states are reasonably placed lower in energy than the E_u state from ^1E_u associated with band III discussed above. In contrast, band I for the Pd(II) complex is assigned to the LMCT S_{lp} → dσ^*, which is logically expected at lower energy than the Sσ → dσ^*, band II. The MCD for this transition is not so easily predicted since it will be a combination of B terms due to at least two unresolved transitions. It is well-known that B term signs depend not only on the orbitals involved in the excited state but also the relative placements of other states that can interact with the state of interest in the presence of the magnetic field.[12] Finally the high-energy shoulder bands IV for Pt(II) and III for Pd(II) are considered. In keeping with the d → p assignments for bands II and III for the Pt(II) complex, band IV is ascribed to the transition to the E_u spin orbit state from $^3A_{2u}$ (5d_{z^2} → 6p_z), which is predicted to have a positive A term. The broad absorption and MCD for band III for the Pd(II) complex is not easily assigned. It is likely an intraligand transition associated with the dto ligand. The free ligand shows absorption in this energy region but with a different MCD. It is not unreasonable to expect the intraligand excitations of the free ligand to be rather significantly modified on coordination, but little more can be concluded from the present measurements.

SCN$^-$ Complexes (Figure 4). Like the dto complexes, the SCN$^-$ complexes of Pt(II) and Pd(II) exhibit rather similar absorption spectra but rather different MCD spectra. With the notion that the Pt(II) complex may exhibit both d → p and LMCT transitions, while the Pd(II) complex can only exhibit LMCT transitions in the accessible energy range, the assignment of the intense bands III (negative A term) in both complexes to the Sσ → dσ^* and band IV (strong positive A term) of the Pt(II) complex to the 5d_{xz}, 5d_{yz} → 6p_z transitions seems reasonable and analogous to the interpretation advanced above for the dto complexes. The unsymmetrical MCD pattern observed for bands III and IV for the Pt(II) complex is reasonably interpreted as the overlap of the negative and positive A terms expected for the Sσ → dσ^* LMCT and d → p E_u states (D_{4h} approximation). The prominent negative A term observed for band III of the Pd(II) complex is expected for the Sσ → dσ^* LMCT. The weaker bands I and II for the Pt(II) complex (see Table I) and I for the Pd(II) complex are assigned to LF transitions and will not be discussed further. Band II for the Pd(II) complex, which is a more intense broad shoulder on band III and has a weak broad positive MCD, may be due to a LMCT involving the nearly nonbonding S lone pairs. Such a transition is expected to be lower in energy than the Sσ → dσ^* transition. An analogous absorption is not resolved for the Pt(II) complex, but there is a positive MCD feature near 3.25 μm^{-1} which may be due to the same process. Band IV, which appears as a broad shoulder absorption in the Pd(II) complex, has an exceptionally weak MCD signal. The assignment of this band is less clear and may be due to an intraligand S_{lp} → π^* transition. An analogus band for the Pt(II) complex would almost certainly be obscured by the intense d → p band IV; the strong MCD for band IV certainly would obliterate any weak MCD feature for such a band. Finally there are broad high-energy absorptions and negative MCD features in the spectra of both the Pd(II) and Pt(II) complexes. These transitions are not clear enough to assign for certain, but they may be due to other unresolved intraligand transitions.[13] The uncomplexed SCN$^-$ ion exhibits charge transfer to solvent (CTTS) bands in this energy region, similar to those exhibited by halide ions such as Br$^-$ and I$^-$.[14] CTTS also is a possibility for coordinated SCN$^-$, but the MCD spectrum for uncomplexed SCN$^-$ is notably different from the broad MCD observed for the complexes at high energy.

Et-Xan$^-$ Complexes (Figures 5 and 6). The spectra for the Ni(II), Pd(II), and Pt(II) Et-Xan$^-$ complexes exhibit more features in both the absorption and MCD than the dto or SCN$^-$ complexes. Apart from some minor changes in resolution, the pattern of the lowest energy bands in the spectra of the three

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Table I. Spectral Data for Acetonitrile Solution

	absorption			MCD		
band no.	$\bar{\nu}$, μm^{-1}	λ, nm	ε, $(M\ cm)^{-1}$	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, $(M\ cm\ T)^{-1}$	assignt
			$[Pt(dto)_2](ClO_4)_2$			
				2.88	+0.011	LF
I	3.15	318	521	3.17	–0.035	LF
				3.74	+0.090	
II	3.79	264	5 140[a] [b]	3.83	0	d → p
				3.90	–0.065	($^3B_1$, ^3E)
				4.24	–2.72	
III	4.34	230	20 700 [b]	4.34	0	d → p
				4.42	+1.95	(^1E)
				4.57	–0.85	
IV	4.62	217	14 300[a] [b]	4.64	0	d → p
				4.73	+0.68	($^3A_2$)
			$[Pd(dto)_2](ClO_4)_2$			
			4 950[a] [b]	2.88	–0.168	
I	3.01	332		3.01	0	$S_{1p} \rightarrow d\sigma^*$
				3.19	+0.305	
II	3.47	288	20 970 [b]	3.38	0	$S\sigma \rightarrow d\sigma^*$
				3.52	–0.189	
				3.81	+0.180	
				4.27	–0.069	intralig?
III	4.86	206	11 100[a]	4.80	–1.47	intralig
			dto			
I	4.82	207	2 900	4.83	+0.29	S Rydb?
			$[(n\text{-}C_4H_9)_4N]_2[Pt(SCN)_4]$			
I	2.47	405	271[a]	2.39	+0.028	LF
II	2.77	361	529			LF
				3.25	+0.32	$S_{1p} \rightarrow d\sigma^*$
				3.75	+1.11	
III	3.84	260	18 600[a] [b]	3.85	0	$S\sigma \rightarrow d\sigma^*$
				4.02	–6.28	
IV	4.11	243	37 500 [b]	4.12	0	d → p
				4.25	+1.32	
				4.51	–2.05	intralig?
V	4.84	206	29 900[a]			intralig
			$[(n\text{-}C_4H_9)_4N]_2[Pd(SCN)_4]$			
I	2.15	465	451[a]	2.08	+0.081	LF
II	2.63	380	1 910[a]	2.63	+0.23	$S_{1p} \rightarrow d\sigma^*$
				3.06	+0.84	
III	3.20	313	26 000 [b]	3.16	0	$S\sigma \rightarrow d\sigma^*$
				3.32	–1.58	
IV	3.73	268	7 500[a]			$S_{1p} \rightarrow \pi^*$lig
				4.32	–1.80	intralig?
V	4.61	217	19 000[a]			intralig
			KSCN			
				4.14	–0.55	
I	4.28	234	3 450 [b]	4.25	0	CTTS
				4.39	+0.67	
				4.68	+0.28	
II	4.95	202	8 670[a]			CTTS
			$Pt(Et\text{-}Xan)_2$			
I	2.24	446	2 630	2.25	+0.62	$S_n \rightarrow d\sigma^*$
II	2.45	408	1 020[a]	2.53	–0.25[a]	$S\pi \rightarrow d\sigma^*$
III	2.81	356	6 630	2.82	–1.31	$S_{1p} \rightarrow d\sigma^*$
				3.22	+0.68	$S_{1p} \rightarrow d\sigma^*$
IV	3.30	303	5 490	3.38	+0.71	$S_{1p} \rightarrow d\sigma^*$
V	3.65	274	8 260[a]	3.60	–1.55	$S_n \rightarrow \pi^*$lig
				3.80	–1.78	$S\sigma \rightarrow d\sigma^*$
VI	4.03	248	40 200	4.06	+3.86	$S\sigma \rightarrow d\sigma^*$
				4.84	–6.42	d → p/π^*lig
VII	5.01	200	35 400	5.09	+0.22	$S\pi \rightarrow p/\pi^*$lig
			$Pd(Et\text{-}Xan)_2$			
I	2.18	458	188	2.16	+0.0065	LF
				2.59	+0.144	$S_n \rightarrow d\sigma^*$
II	2.63	380	4 080	2.80	–0.152	$S\pi \rightarrow d\sigma^*$
				3.07	+0.40	$S_{1p} \rightarrow d\sigma^*$
				3.22	–0.64	$S_{1p} \rightarrow d\sigma^*$
				3.37	–0.58	$S\sigma \rightarrow d\sigma^*$
III	3.52	284	45 500	3.55	+2.19	$S\sigma \rightarrow d\sigma^*$
IV	4.21	238	18 800	4.22	–4.23	$S\pi \rightarrow \pi^*$lig
V	4.58	218	7 700	4.62	+1.02	intralig?
VI	4.90	204	14 200[a]			intralig?
VII	5.15	194	19 500[a]	5.12	–3.99	d → π^*/p?
			$Ni(Et\text{-}Xan)_2$			
I	2.10	476	1 260	2.12	+0.83	$S_n \rightarrow d\sigma^*$
				2.29	–0.75[a]	$S\pi \rightarrow d\sigma^*$
II	2.41	414	2 390	2.39	–1.52	$S_{1p} \rightarrow d\sigma^*$
III	2.58	387	1 140[a]	2.60	+0.055	$S_{1p} \rightarrow d\sigma^*$
				2.84	+0.101	$S_{1p} \rightarrow d\sigma^*$
IV	3.17	316	41 250	3.09	+0.158	$S\sigma \rightarrow d\sigma^*$
				3.43	+3.38	$S\sigma \rightarrow d\sigma^*$
				3.78	–1.50	$S_n \rightarrow \pi^*$lig
V	3.98	251	25 980	4.14	–2.60	$S\pi \rightarrow \pi^*$lig
VI	4.59	218	48 400	4.55	–9.89	d → π^*/p
				4.89	+2.93	d → π^*/p?
			K[Et-Xan]			
				2.32	-3.7×10^{-4}	$S_n \rightarrow \pi^*$
I	2.53	396	43.4	2.50	$+2.4 \times 10^{-4}$	$S_n \rightarrow \pi^*$
II	3.22	310	21 500	3.22	–0.525	$S\pi \rightarrow \pi^*$
				3.42	+0.093	?
III	3.82	262	2 190[a]	3.90	–0.197	?
IV	4.40	227	11 120	4.43	–0.382[a]	CTTS?
V	4.71	212	12 000	4.95	–0.77	CTTS?

[a] Shoulder. [b] Pseudo-A term.

complexes is remarkably similar and displays an energy ordering of Ni(II) < Pd(II) < Pt(II). This order is suggestive of LMCT transitions with the shift following the metal orbital stability. The most prominent absorption (band VI for the Pt(II) complex, band III for the Pd(II) complex, and band IV for the Ni(II) complex) is logically assigned to $S\sigma \rightarrow d\sigma^*$ and nicely illustrates the trend. The MCD for this transition shows a fairly complex pattern but can be visualized as an unsymmetrical pseudo-A term with a positive feature slightly higher in energy than the absorption maximum. The two B terms that comprise the pseudo-A term are consistent with the two allowed $S\sigma \rightarrow d\sigma^*$ LMCT excitations which give rise to in-plane polarized B_{3u} and B_{2u} excited states, respectively (assuming molecular symmetry of D_{2h}). The remaining two $S\sigma \rightarrow d\sigma^*$ excited states are parity forbidden (A_g and B_{1g}) and are expected to be substantially weaker and will certainly be obscured by these intense bands. If these assignments are accepted, then several weaker ($1000 < \epsilon < 10\,000$ M^{-1} cm^{-1}) bands are expected to lower energy which can be ascribed to S_n, S_{1p}, or $S\pi \rightarrow d\sigma^*$ excitations. On the basis of intensity, bands I–IV for the Pt(II) complex are assigned as $S_n \rightarrow d\sigma^*$ (allowed out-of-plane polarized, B_{1u}), $S\pi \rightarrow d\sigma^*$ (forbidden, A_u), and the two allowed $S_{1p} \rightarrow d\sigma^*$ (in-plane polarized, B_{3u} and B_{2u}), respectively. The two positive features in the MCD (at 3.22 and 3.38 μm^{-1}) associated with band IV suggest more than one transition in this region. One additional possibility is the presence of an excitation to a $S_{1p} \rightarrow d\sigma^*$ state that is formally parity forbidden (B_{1g} for example). For the Ni(II) complex analogous assignments of band I, the negative MCD shoulder at 2.29 μm^{-1}, and bands II and III can be visualized for the low-energy LMCT transitions. Here bands II and III are interpreted as the two allowed $S_{1p} \rightarrow d\sigma^*$ transitions. However for the Pd(II) complex band I seems too weak to be a LMCT transition and, therefore, is assigned as a LF band. Unfortunately band II for the Pd(II) complex is rather broad and unresolved, but the MCD pattern is similar to that for bands I–III in the Pt(II) complex spectrum. Therefore it seems likely that band II and the MCD features at 2.59, 2.80, 3.07, and 3.22 μm^{-1} for the Pd(II) complex are due to S_n, $S\pi$, and $S_{1p} \rightarrow d\sigma^*$ LMCT.

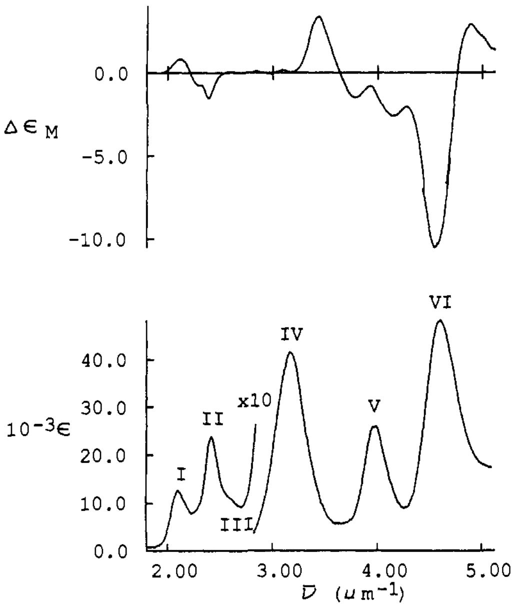

Figure 6. Electronic absorption (lower curves) and MCD (upper curves) for Ni(Et-Xan)$_2$ in acetonitrile. Units are as in Figure 3.

Band V for the Pt(II) complex presents a rather poorly resolved shoulder and a broad negative MCD feature near 3.6 μm^{-1}. A similar broad negative MCD is observed for the Ni(II) complex at 3.78 μm^{-1}, but no clear absorption band is resolved. If a spectral feature were to occur at similar energies for the Pd(II) complex, it would surely be obscured by the strong absorption band III and its associated positive MCD. The appearance of bands that seem to be independent of the metal ion would be consistent with a ligand-localized transition. Energetically an $S_n \rightarrow \pi^*$ ligand excitation (B_{3u} excited state in the D_{2h} approximation) would be expected in this region. The $n \rightarrow \pi^*$ character of the transition would explain its low intensity, whereas the MCD B term could arise from magnetic coupling with a number of higher energy intraligand excitations involving the π^* orbital. Another higher energy set of bands that seem to be independent of the metal ion consists of band IV at 4.22 μm^{-1} for the Pd(II) complex and band V at 4.14 μm^{-1} for the Ni(II) complex. Each has a strong negative MCD and shows a fairly intense absorption. A reasonable assignment for these bands is to an $S\pi \rightarrow \pi^*$ ligand-localized transition. If this assignment is correct, then a natural question arises as to why a similar band is not observed near the same energy in the spectrum of the Pt(II) complex. Band VI for the Pt(II) complex has already been assigned as the intense $S\sigma \rightarrow d\sigma^*$ as noted above. The only remaining feature to higher energy is band VII at 5.01 μm^{-1}, which shows a very strong negative MCD feature at slightly lower energy (4.84 μm^{-1}) and, thus, seems noticeably different from the bands assigned as $S\pi \rightarrow \pi^*$ for the Ni(II) and Pd(II) complexes near 4.2 μm^{-1}. In keeping with the assignments of a d → p transition in this energy region for the Pt(II) dto and SCN$^-$ complexes, such a transition would be expected here for the Et-Xan$^-$ complex. However in this case the $6p_z$ Pt(II) orbital would be expected to interact to a significant extent with the out-of-plane ligand π^* orbitals, and thus the empty orbital involved in the excitation would have both 6p and π^* ligand contributions. Accordingly band VII for the Pt(II) complex may be interpreted as a combination of $d \rightarrow p/\pi^*$ ligand and $S\pi \rightarrow p/\pi^*$ ligand. The very strong MCD seems to be characteristic of the d → p type excitation. Band VI at 4.59 μm^{-1} for the Ni(II) complex is quite similar in appearance to band VII for the Pt(II) complex; the very strong negative MCD is also analogous. Therefore, a similar assignment is adopted in this case. It should be noted however that the 4p orbitals of Ni(II) are relatively higher in energy than the 3d compared to the 6p and 5d of Pt(II), so that the empty molecular orbital should be visualized as having a greater ligand π^* contribution than 4p, and therefore the transition in the Ni(II) complex will have a greater metal to ligand charge-transfer (MLCT) character than in the case of the Pt(II) complex. There is a parallel in the Pt(II) and Ni(II) $M(CN)_4^{2-}$ complexes,[15] where MLCT and d → p assignments have also been made. It is noteworthy in this case that the energies for the lowest absorptions for transitions of this type show the trend Pt(II) ≈ Ni(II) < Pd(II). If the parallelism holds for the Et-Xan$^-$ complexes, then the $d \rightarrow p/\pi^*$ transitions for the Pd(II) complex may lie to higher energy than for the Ni(II) and Pt(II) complexes and therefore would not be within the range of the present measurements. Finally, bands V–VII for the Pd(II) complex appear as broad high-energy absorptions and difficult to assign specifically. They may be some type of intraligand transition or band VII may be MLCT and due to a $d \rightarrow \pi^*/p$ transition. The strong negative MCD seems consistent with the latter notion.

Spectral data for the uncomplexed Et-Xan$^-$ ligand are also included in Table I. The assignments given for bands I and II have been advanced by others.[16] The MCD shows that band I must contain at least two transitions because of the two opposite signed B terms. The low intensity is consistent with the $n \rightarrow \pi^*$ transition. Band II exhibits a much stronger (negative) B term and higher absorption intensity characteristic of the $\pi \rightarrow \pi^*$ transition. The higher energy absorptions and their associated MCD may be due to intraligand transitions or they may be due to CTTS, but the present study does not offer any basis for a detailed assignment.

Concluding Remarks. The interpretation of the absorption and MCD spectra for the dto, SCN$^-$, and Et-Xan$^-$ complexes advanced above is summarized in Table I. The prominent intense $S\sigma \rightarrow d\sigma^*$ transitions follow the energetic trend Pt(II) > Pd(II) > Ni(II) characteristic of LMCT transitions that depend upon metal orbital stability. It is interesting that the energy of the $S\sigma \rightarrow d\sigma^*$ transition does not vary much among the three ligand types studied here. For example the $S\sigma \rightarrow d\sigma^*$ bands occur at 3.47, 3.20, and 3.52 μ^{-1} for the Pd(II) dto, SCN$^-$, and Et-Xan$^-$ complexes, respectively. This behavior suggests that the ligands have similar σ-donor ability toward the metal ion. The small differences that are observed may simply reflect electron repulsion differences or minor differences in ligand orbital stability. The notion that the dto and SCN$^-$ ligands act as predominantly σ-donors with very little tendency toward π bonding also finds a basis in the spectral assignments. The spectra differ from the spectra of MX_4^{2-} halide complexes where π-LMCT and σ-LMCT band systems separated by 0.8–1.2 μm^{-1} have been identified.[1,2b] In the case of the Pt(II) complexes, the notable differences observed in the MCD spectra in the 3.8–5.0-μm^{-1} region compared to the Pd(II) complexes are attributable to 5d → 6p metal-localized transitions. The value of the MCD spectra here is clearly evident because the pattern of the absorption spectra for the Pt(II) and Pd(II) dto and SCN$^-$ complexes is deceptively similar. Finally, the Et-Xan$^-$ complexes show fairly complex LMCT spectra which can be attributed to the unsaturated nature of the ligand with excitations from nonbonding, lone pair, π, and σ orbitals on the S donor atoms. In this case some intraligand transitions were also identified, which is perhaps not surprising in view of the strong absorptions of the uncomplexed ligands found in the same energy region as the LMCT in the complexes.

Acknowledgment is made to the NATO Scientific Affairs Division and the Middle East Technical University Research Fund for support of this work.

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