the bridge protons. However, there seems to be at least some covalent character in the bonds that coordinate the oxygen atoms to the uranyl group and for that reason there is no basis for a quantitative assignment of charge to the uranyl group. There is not any obvious experiment for rigorously separating what might be termed electronic and electric field contributions to $\Delta\sigma$. The closest approach to such an experimental separation of effects is to examine the chemical shifts for adducts that are formed with other metal nitrates. If these metal ions are magnetically isotropic, then the observed shifts must be exclusively due to what we have termed electronic and electric field contributions. The data in Table I for the adducts with lanthanum and thorium nitrates indicate that these contributions may be the lesser fraction of the total. It should be noted that due to the possibility of a large charge on thorium and lanthanum the electric field effect should be even larger than with uranium.

The discussion to this point has also ignored the possible role of the nitrate ions. In the main, this oversight is permissible in a first approximation. The nitrate ion is magnetically anisotropic but $\Delta\chi_{\text{atomic}}$ is only 8×10^{-30}.[11]

Another possible weakness in our explanation is that the uranyl ion may not be strictly linear in all circumstances. While there is considerable evidence for linearity,[12] especially in crystals,[13] there is also some evidence for a bent uranyl ion.[14,15]

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CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE AND THE
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The Electronic Structures and Spectral Properties of the Square-Planar Dithiooxalate Complexes of Nickel(II), Palladium(II), Platinum(II), and Gold(III)

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Received December 21, 1964

The electronic spectra of the dithiooxalate (dto^{2-}) complexes of Ni(II), Pd(II), Pt(II), and Au(III) are assigned on the basis of the derived energy levels for the $Ni(dto)_2^{2-}$ complex. These assignments are compared to those proposed earlier for the analogous complexes containing maleonitriledithiolate (mnt^{2-}). The analysis indicates that d → d, charge-transfer, and intra-ligand transitions occur below 50,000 cm.$^{-1}$ in these complexes. The Δ_1 values ($x^2 - y^2 \leftrightarrow xy$ separation) of the dto^{2-} complexes are compared to the Δ_1 values of complexes containing related sulfur-donor ligands.

Introduction

The interpretation of the electronic spectra of planar metal complexes has been a subject of considerable recent interest.[3] For d^8 low-spin complexes containing halide ligands, the charge-transfer bands are of the ligand → metal (L → M) type, while planar complexes containing diatomic ligands with some π-acceptor capability show reasonably low-energy charge-transfer bands of the metal → ligand (M → L) type. For example, $Ni(CN)_4^{2-}$ shows three fairly intense bands between 32,000 and 37,600 cm.$^{-1}$ which are assigned metal(d) → $CN(\pi^*)$.[4] It is obviously desirable to attempt a classification of the electronic spectra of planar complexes containing ligands which themselves have low-energy absorption bands, indicating a small spacing between the highest filled and the lowest empty levels. In such cases, we may possibly encounter absorption bands due to four different types of transitions: d → d, L → M, M → L, and transitions mainly localized in the ligand system which we shall abbreviate L → L*. Some progress has been made in the interpretation of such complicated spectra, as for example in the planar maleonitriledithiolate complexes[5] and in the four-coordinate β-diketone complexes of Cu(II).[6] In this paper, we shall attempt to interpret the complete electronic spectra of planar $M(dto)_2^{n-}$ (M = Ni(II), Pd(II), Pt(II), and Au(III)) complexes in terms of d → d, L → M, M → L, and L → L* transitions using a molecular orbital theory basis for the detailed assignment scheme.

Experimental

Preparation of Compounds.—Potassium dithiooxalate was obtained from Eastman Kodak and was used as received. The

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(3) Pertinent references are found in the following review: H. B. Gray, *Progr. Transition Metal Chem.*, **1**, in press.

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$K_2Ni(dto)_2$, $K_2Pd(dto)_2^{2-}$, and $K_2Pt(dto)_2$ complexes were prepared in the manner described by Cox, Wardlaw, and Webster.[7] The $KAu(dto)_2$ complex was prepared in a similar manner and was found to be very unstable to air, heat, and light. It was prepared and kept at 0° under nitrogen and in the dark. A typical $[(n\text{-}C_4H_9)_4N]_2[M(dto)_2]$ complex (M = Ni, Pd, Pt) was prepared by adding a 50% aqueous ethanol solution of $(n\text{-}C_4H_9)_4NBr$ to an aqueous solution of the $K_2M(dto)_2$ complex. Stoichiometric quantities were used. The $[(n\text{-}C_4H_9)_4N]_2[M(dto)_2]$ complex, which immediately precipitated, was recrystallized from ethanol–water mixtures. The composition of the complexes was established by elemental analyses.

Physical Measurements.—Electronic spectra were taken using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used as received. Water used in spectral determinations was distilled and run through an anion–cation-exchange resin. Static susceptibility measurements were performed at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. All the complexes described above were found to be diamagnetic.

Structure of the dto^{2-} Complexes.—The Ni(II), Pd(II), and Pt(II) complexes are diamagnetic and have been shown to be square-planar.[7] The Au(III) complex is diamagnetic and is also undoubtedly square-planar.

Molecular Orbital Theory

The molecular orbitals for $Ni(dto)_2^{2-}$ were calculated in the same manner as those for $Ni(mnt)_2^{2-}$.[5] The wave functions and Coulomb integrals used for Ni in the $Ni(mnt)_2^{2-}$ calculation were used unaltered in the $Ni(dto)_2^{2-}$ calculation. The in-plane σ and π_h ligand functions from the $Ni(mnt)_2^{2-}$ calculation were also taken, with some alteration to be consistent with the dto^{2-} π_v orbitals perpendicular to the molecular plane. The π_v functions were obtained from a separate calculation. The symmetries and energies of the calculated levels are given in Table I. The relative energies of the most important levels are shown in Figure 1. The ground state of $Ni(dto)_2^{2-}$ is $\ldots(3b_{2g})^2(3b_{3g})^2(4a_g)^2 = {}^1A_g$. The highest filled "metal" levels have $3b_{3g}(yz)$, $4a_g(x^2 - y^2)$, and $3b_{2g}(xz)$ symmetries, with the calculated ordering $4a_g(x^2 - y^2), 3b_{3g}(yz) > 3b_{2g}(xz)$. However, as will be discussed later, the ordering deduced from M → L(π^*) band intensities is $4a_g(x^2 - y^2) > 3b_{3g}(yz) \approx 3b_{2g}(xz)$. Thus we have indicated $4a_g(x^2 - y^2)$ above $3b_{3g}(yz)$ and $3b_{2g}(xz)$ in Figure 1. The empty metal level is of $3b_{1g}(xy)$ symmetry and is strongly σ-antibonding. We expect that the three d → d type transitions $4a_g(x^2 - y^2), 3b_{3g}(yz), 3b_{2g}(xz) \rightarrow 3b_{1g}(xy)$ will be of nearly the same energy. Further, we expect closely spaced M → L(π^*) bands $4a_g(x^2 - y^2) \rightarrow 3b_{1u}$, $3b_{3g}(yz) \rightarrow 3b_{1u}$, and $3b_{2g}(xz) \rightarrow 3b_{1u}$, and two L → M bands, $L(\pi) \rightarrow 3b_{1g}(xy)$ and $L(\sigma) \rightarrow 3b_{1g}(xy)$ spaced by *ca.* 10,000 cm.$^{-1}$ as found in the planar halides and in the electronically similar mnt^{2-} complexes.[5] Finally, the $L(\pi) \rightarrow L(\pi^*)$ band in the complexes is expected to be found slightly shifted from its position in the free ligand.

TABLE I

CALCULATED ORBITAL ENERGIES FOR $Ni(dto)_2^{2-}$ [a]

MO	Orbital energy, 10^3 cm.$^{-1}$	MO	Orbital energy, 10^3 cm.$^{-1}$
$3b_{2u}$	133.4	$2b_{3u}$	−107.1
$3b_{3u}$	88.6	$2b_{2u}$	−107.1
$5a_g$	52.0	$2b_{1u}$	−108.6
$4b_{1u}$	−13.1	$2a_g$	−113.4
$3a_u$	−34.0	$2b_{3g}$	−113.5
$4b_{3g}$	−39.7	$2b_{2g}$	−114.2
$4b_{2g}$	−71.9	$1b_{3u}$	−117.0
$3b_{1u}$	−71.8	$1b_{2u}$	−117.0
$3b_{1g}$	−75.2	$1b_{1g}$	−132.6
$3b_{3g}$	−96.2	$1a_g$	−145.0
$4a_g$	−96.5	$1b_{3g}$	−170.6
$3b_{2g}$	−97.5	$1a_u$	−170.6
$3a_g$	−103.2	$1b_{2g}$	−193.6
$2a_u$	−107.1	$1b_{1u}$	−193.7
$2b_{1g}$	−107.1		

[a] The calculation was carried out on the Columbia IBM 7094, using a program written by P. T. Manoharan. The x axis bisects the two C–C lines in $Ni(dto)_2^{2-}$ and the z axis is perpendicular to the molecular plane.

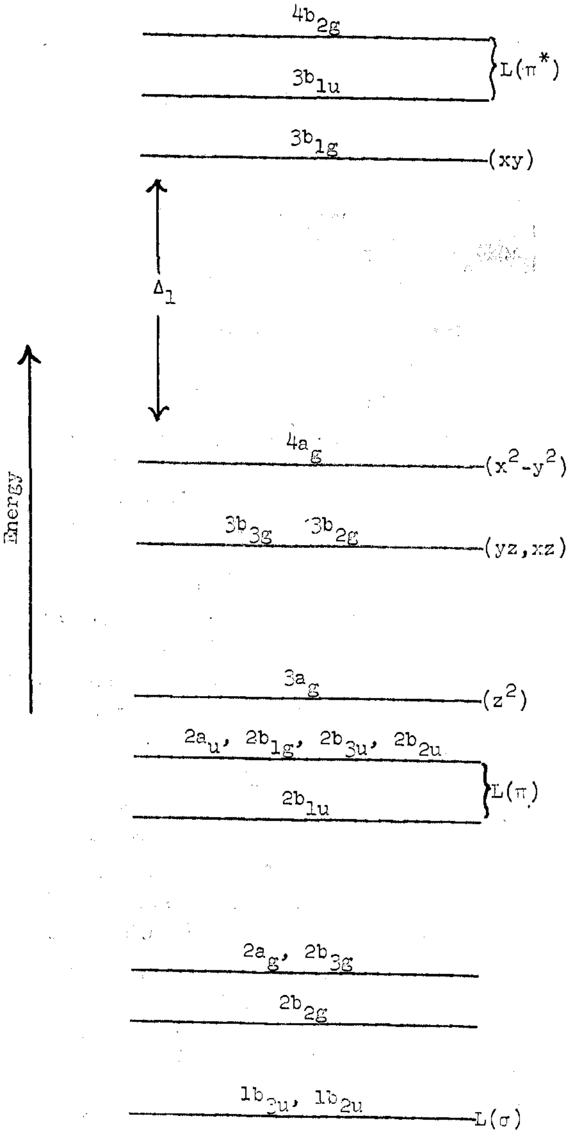

Figure 1.—Schematic diagram of the relative energies of the spectroscopically important molecular orbitals of $Ni(dto)_2^{2-}$. The x axis bisects the two C–C lines and the z axis is perpendicular to the molecular plane.

The band positions in such a complex spectrum are not independent. We formulate as a useful relationship the following simple equation connecting the posi-

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(7) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

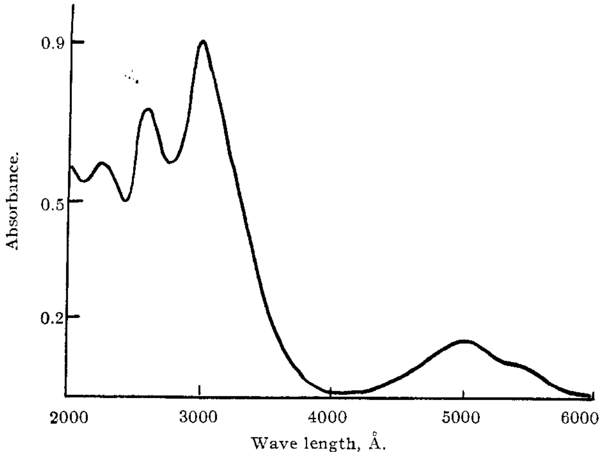

Figure 2.—Absorption spectrum of $[(n\text{-}C_4H_9)_4N]_2[Ni(dto)_2]$, 3.90×10^{-5} *M* in acetonitrile solution; 1-cm. cell path length.

tion of the L → L* band with the positions of the lowest L → M, M → L, and d → d bands. For low-spin complexes

$$\bar{\nu}(\mathrm{L} \rightarrow \mathrm{L}^*) = \bar{\nu}(\mathrm{L} \rightarrow \mathrm{M}) + \bar{\nu}(\mathrm{M} \rightarrow \mathrm{L}^*) - \bar{\nu}(\mathrm{d} \rightarrow \mathrm{d}) + \mathrm{e.r.} \quad (1)$$

The e.r. term in eq. 1 is the difference in the interelectronic-repulsion energies of the four excited states involved and must be set from experiment for one complex in an analogous series. We assume that the e.r. term will be nearly constant in a series of electronically similar complexes.

Spectral Properties of the dto^{-2} Complexes

It should be noted that the electronic spectral properties of the planar dto^{2-} complexes are essentially the same in water, pyridine, acetone, dimethylformamide, and acetonitrile. This indicates that axial solvent perturbations are of minor importance in these cases. The aqueous solution spectra agree with those found previously.[8]

Electronic Spectrum of $Ni(dto)_2^{2-}$.—The electronic spectrum of $Ni(dto)_2^{2-}$ in acetonitrile is shown in Figure 2. There are five maxima in the region between 16,000 and 50,000 cm.$^{-1}$; all five of the bands are quite intense and must be due to allowed transitions. In addition to the five maxima, there is a shoulder at 17,700 cm.$^{-1}$. The spectral assignments, consistent with the remarks in the theory section, are given in Table II. Calculated transition energies are given for comparison.

L(π) → L(π^*) Band.—The first $\pi \rightarrow \pi^*$ band in the spectrum of diethyldithiooxalate in acetonitrile is at 35,600 cm.$^{-1}$. This band in Na_2dto in aqueous solution appears at 39,100 cm.$^{-1}$. Thus we assign the band with a maximum at 38,600 cm.$^{-1}$ in $Ni(dto)_2^{2-}$ to the L(π) → L(π^*) transitions. The detailed assignment is $^1A_g \rightarrow {}^1B_{1u}, {}^1B_{2u}, {}^1B_{3u}(2b_{3u}, 2a_u, 2b_{1u} \rightarrow 4b_{2g})$ with an average calculated one-electron energy of 36,600 cm.$^{-1}$. The calculated one-electron energy is in good agreement with the experimental band energy.

TABLE II

THE ELECTRONIC SPECTRUM OF $Ni(dto)_2^{2-}$ [a]

Band maxima, cm.$^{-1}$	$\epsilon \times 10^{-3}$	Assignments	Calcd. energies, cm.$^{-1}$
(17,700) sh	1.3	$^1A_g \rightarrow {}^1B_{1g}\ (4a_g \rightarrow 3b_{1g})$	18,500[b]
		$^1A_g \rightarrow {}^1B_{1u}\ (4a_g \rightarrow 3b_{1u})$	24,800
19,900	3.7	$^1A_g \rightarrow {}^1B_{2u},{}^1B_{3u}$ $(3b_{3g},3b_{2g} \rightarrow 3b_{1u})$	25,150[c]
33,400	24.0	$^1A_g \rightarrow {}^1B_{1u},{}^1B_{2u},{}^1B_{3u}$ $(2b_{2u},2b_{3u},2a_u \rightarrow 3b_{1g})$	31,900
38,600	18.8	$^1A_g \rightarrow {}^1B_{1u},{}^1B_{2u},{}^1B_{3u}$ $(2b_{3u},2a_u,2b_{1u} \rightarrow 4b_{2g})$	36,600[c]
44,400	16.7	$^1A_g \rightarrow {}^1B_{3u},{}^1B_{2u}$ $(1b_{2u},1b_{3u} \rightarrow 3b_{1g})$	41,900

[a] Measured in acetonitrile solutions of $[(n\text{-}C_4H_9)_4N]_2[Ni(dto)_2]$. [b] Corrected for interelectronic-repulsion energy using $F_2 = 10F_4 = 800$ cm.$^{-1}$. [c] Average of the one-electron transition energies.

Charge-Transfer Bands.—Recalling that the M → L charge-transfer transitions in $Ni(CN)_4^{2-}$ form a closely-spaced three-band system[4] and those in $Ni(mnt)_2^{2-}$ a two-band system,[5] we assign the maximum at 19,900 cm.$^{-1}$ and the shoulder at 17,700 cm.$^{-1}$ to these transitions in $Ni(dto)_2^{2-}$. Although all three low-energy M → L(π^*) transitions ($4a_g(x^2 - y^2)$, $3b_{3g}(yz)$, $3b_{2g}(xz) \rightarrow 3b_{1u}$) are formally allowed, $4a_g(x^2 - y^2) \rightarrow 3b_{1u}$ alone is "perpendicular" and is expected to give rise to a weaker absorption band. The similar $4a_g(x^2 - y^2) \rightarrow$ L(π^*) band in $Ni(mnt)_2^{2-}$ is orbitally forbidden.[5] Thus we assign the shoulder at 17,700 cm.$^{-1}$ as $^1A_g \rightarrow {}^1B_{1u}(4a_g(x^2 - y^2) \rightarrow 3b_{1u})$ and the maximum at 19,900 cm.$^{-1}$ as $^1A_g \rightarrow {}^1B_{2u},{}^1B_{3u}(3b_{3g}(yz), 3b_{2g}(xz) \rightarrow 3b_{1u})$. This gives the one-electron ordering $4a_g(x^2 - y^2) > 3b_{3g}(yz), 3b_{2g}(xz)$, as shown in Figure 1.

The two bands at 33,400 and 44,400 cm.$^{-1}$, separated by 11,000 cm.$^{-1}$, are logically assigned as typical L → M charge transfer. The calculated one-electron energies are 31,900 and 41,900 cm.$^{-1}$, respectively. In $Ni(mnt)_2^{2-}$ and in planar tetrahalides, the first L → M band is less intense than the second,[4] but in $Ni(dto)_2^{2-}$ the reverse is true. A possible explanation for the reversal in $Ni(dto)_2^{2-}$ is that there are three allowed transitions in the band at 31,900 cm.$^{-1}$, as compared with two in the first L → M band in $Ni(mnt)_2^{2-}$.[5]

d → d Type Bands.—Since all d → d transitions in centrosymmetric complexes are parity forbidden, it is very likely that no observed maximum in the $Ni(dto)_2^{2-}$ spectrum is of the d → d type. It is known that the first spin-allowed band in a low-spin square-planar Ni(II) complex occurs at about the same energy as the first spin-allowed band in the corresponding octahedral, low-spin Co(III) complex.[9] Thus from the Δ_0 reported by Carlin and Canziani for $Co(dto)_3^{3-}$,[10] we may tentatively place the first d-d band in $Ni(dto)_2^{2-}$ at 17,700 cm.$^{-1}$. Thus we suggest that the shoulder at 17,700 cm.$^{-1}$ contains the $4a_g(x^2 - y^2) \rightarrow 3b_{1g}(xy)$ d-d transition. The calculated position of the $4a_g(x^2 - y^2) \rightarrow 3b_{1g}(xy)$ band, corrected for interelectronic-repulsion energy, is 18,500 cm.$^{-1}$.

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(9) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon-Addison-Wesley, Reading, Mass., 1962, p. 123.

(10) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).

TABLE III

ELECTRONIC SPECTRA OF $M(dto)_2^{n-}$ COMPLEXES WITH A $\ldots(3b_{3g})^2(4a_g)^2 = {}^1A_g$ GROUND STATE [a]

Transitions	Complexes (band ϵ in parentheses)			
	$Ni(dto)_2^{2-}$	$Pd(dto)_2^{2-}$	$Pt(dto)_2^{2-}$	$Au(dto)_2^{-}$ [b]
d → d type				
${}^1A_g \rightarrow {}^1B_{1g}(x^2 - y^2 \rightarrow xy)$	17,700 (1,300)[c]	*d*	30,000 (1,000)	*d*
$L(\pi) \rightarrow L(\pi^*)$				
${}^1A_g \rightarrow {}^1B_{1u},{}^1B_{2u},{}^1B_{3u}$	38,600 (18,000)	41,300 (17,000)	41,700 (26,000)	41,500 (?)[c]
L → M charge transfer				
${}^1A_g \rightarrow {}^1B_{1u},{}^1B_{2u},{}^1B_{3u}(L(\pi) \rightarrow M)$	33,400 (24,000)	25,100 (7,200)	45,500 (25,000)	36,500 (16,000)
${}^1A_g \rightarrow {}^1B_{2u},{}^1B_{3u}(L(\sigma) \rightarrow M)$	44,400 (16,000)	36,400 (42,000)	*d*	*d*
$M \rightarrow L(\pi^*)$ charge transfer				
${}^1A_g \rightarrow {}^1B_{1u}$	17,700 (1,300)[c]	*d*	21,600 (2,500)	31,000 (?)[c]
${}^1A_g \rightarrow {}^1B_{2u}$	19,900 (3,700)	*d*	23,100 (?)[c]	*d*
${}^1A_g \rightarrow {}^1B_{3u}$	19,900 (3,700)	*d*	23,400 (8,500)	*d*

[a] Maxima in cm.$^{-1}$ for spectra in acetonitrile solutions of $[(n\text{-}C_4H_9)_4N]_2[M(dto)_2]$. [b] Spectrum of $KAu(dto)_2$ in acetonitrile. [c] Shoulder. [d] Not observed.

To summarize, the observed electronic spectrum of $Ni(dto)_2^{2-}$ is composed of a d → d band, two L → M charge-transfer bands, the $M \rightarrow L(\pi^*)$ band system, and the $L(\pi) \rightarrow L(\pi^*)$ transition which is known to be present in dto^{2-} and diethyl dithiooxalate.

Electronic Spectra of $Pd(dto)_2^{2-}$, $Pt(dto)_2^{2-}$, and $Au(dto)_2^{-}$.—The band maxima in the electronic spectra of $Pd(dto)_2^{2-}$, $Pt(dto)_2^{2-}$, and $Au(dto)_2^{-}$ are given in Table III. The spectra of these three complexes are similar to that of $Ni(dto)_2^{2-}$ and may be assigned accordingly. Again each band will be discussed as to type.

$L(\pi) \rightarrow L(\pi^*)$ Bands.—The bands at 41,300 cm.$^{-1}$ in $Pd(dto)_2^{2-}$, at 41,700 cm.$^{-1}$ in $Pt(dto)_2^{2-}$, and the intense shoulder at 41,500 cm.$^{-1}$ in $Au(dto)_2^{-}$ are assigned to internal ligand transitions. These bands are shifted to slightly higher energies from the transition at 39,100 cm.$^{-1}$ in Na_2dto. The extinction coefficients of these bands are up to two times as large as the ϵ for dto^{2-} itself. This is a reasonable result since each molecule is composed of two dto^{2-} ligands.

Charge-Transfer Bands.—In the case of $Pd(dto)_2^{2-}$, the $M \rightarrow L(\pi^*)$ band is probably covered by the very intense L → M band at 36,400 cm.$^{-1}$. In $Pt(dto)_2^{2-}$, on the other hand, a suggestive three-band system is very evident. These bands, at 21,600, 23,100, and 23,400 cm.$^{-1}$, are thus assigned to $M \rightarrow L(\pi^*)$ charge transfer. The shoulder at 31,000 cm.$^{-1}$ in $Au(dto)_2^{-}$ is assigned as the lowest of its $M \rightarrow L(\pi^*)$ transitions. It is important to note that the ordering of these transitions follows the order found in $M(CN)_4^{n-}$ complexes for M → L transitions, Ni(II) < Pd(II) > Pt(II) < Au(III).[4]

The band in $Pd(dto)_2^{2-}$ at 26,000 cm.$^{-1}$ is interpreted as the $L(\pi) \rightarrow M$ band, while the band *ca.* 10,000 cm.$^{-1}$ away, at 36,400 cm.$^{-1}$, is interpreted as the $L(\sigma) \rightarrow M$ band. This behavior parallels that of $Ni(dto)_2^{2-}$ and of the planar mnt^{2-} and halide complexes mentioned previously. In $Au(dto)_2^{-}$, the band at 36,500 cm.$^{-1}$ is assigned as $L(\pi) \rightarrow M$ transitions. The $L(\sigma) \rightarrow M$ band in $Au(dto)_2^{-}$ apparently falls beyond our measured range. For $Pt(dto)_2^{2-}$, only the band at 45,500 cm.$^{-1}$ remains unassigned. It is interpreted as the $L(\pi) \rightarrow M$ transitions. These bands also follow the accepted energy ordering for L → M bands, Ni(II) > Pd(II) < Pt(II) > Au(III).[4]

d → d Type Bands.—Using the above $L(\pi) \rightarrow L(\pi^*)$ and charge-transfer assignments, along with a calculated e.r. term of 5200 cm.$^{-1}$ for $Ni(dto)_2^{2-}$, eq. 1 was solved for the predicted energies of the d–d bands of the remaining complexes. The predicted energy of the $4a_g(x^2 - y^2) \rightarrow 3b_{1g}(xy)$ band for $Pt(dto)_2^{2-}$ is 30,500 cm.$^{-1}$. For this reason, the relatively weak band in $Pt(dto)_2^{2-}$ at 30,000 cm.$^{-1}$ is assigned as the $4a_g(x^2 - y^2) \rightarrow 3b_{1g}(xy)$ transition. From the observed[5] increase in Δ_1 in going from $Ni(mnt)_2^{2-}$ to $Pt(mnt)_2^{2-}$, we estimate a value of 26,000 cm.$^{-1}$ for the $4a_g(x^2 - y^2) \rightarrow 3b_{1g}(xy)$ band in $Pd(dto)_2^{2-}$. Thus the band falls under the intense $L(\pi) \rightarrow M$ band at 26,000 cm.$^{-1}$ and cannot be directly observed. The estimated d → d band position in $Pd(dto)_2^{2-}$ gives a value for the first $M \rightarrow L(\pi^*)$ transition of 36,100 cm.$^{-1}$, which adds some support to the suggestion that both $L(\sigma) \rightarrow M$ and $M \rightarrow L(\pi^*)$ transitions occur at this energy. This is one reasonable explanation of the anomalously high intensity of the 36,400 cm.$^{-1}$ band in $Pd(dto)_2^{2-}$.

In summary, the $Pd(dto)_2^{2-}$ spectrum is seen to have three intense bands: one $L(\pi) \rightarrow L(\pi^*)$ and two L → M. The d → d and $M \rightarrow L(\pi^*)$ bands are obscured by the more intense L → M bands. The $Pt(dto)_2^{2-}$ complex exhibits a rich spectrum interpreted as one $L(\pi) \rightarrow L(\pi^*)$ band, one L → M band, three closely spaced $M \rightarrow L(\pi^*)$ bands, and one d → d band. The $Au(dto)_2^{-}$ complex shows the $L(\pi) \rightarrow L(\pi^*)$ band and only one each of the L → M and $M \rightarrow L(\pi^*)$ bands. Both $M \rightarrow L(\pi^*)$ and L → M energy trends are consistent with previously established orders.

Discussion

We have shown that all of the bands in the spectra of $Ni(dto)_2^{2-}$, $Pd(dto)_2^{2-}$, $Pt(dto)_2^{2-}$, and $Au(dto)_2^{-}$ may be assigned consistently using the molecular-orbital levels calculated for $Ni(dto)_2^{2-}$. From these assignments we are now able to place dto^{2-} in the planar spectrochemical series and compare its position with the positions of other bidentate sulfur-donor ligands.

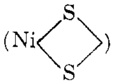
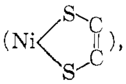
Planar Spectrochemical Series of Sulfur-Donor Ligands.—From the position of the first electronic band, the Δ_1 values for a number of MS_4 (M = Ni(II), Pd(II), Pt(II)) complexes are given in Table IV. The planar NiS_4 spectrochemical series is as follows: $mnt^{2-} < (CF_3)_2C_2S_2^{2-} < dtp^- < exan^- < dtc^- < dmp^{2-} < dtm^- \sim dto^{2-}$. The spectrochemical position of mnt^2 is consistently lowest in the Ni(II), Pd(II), and Pt(II) complexes, while dto^{2-} is consistently highest. The large variation in ligand-field strength in the NiS_4 complexes is quite striking and is probably due to a combination of geometric and electronic factors. In general, the four-membered ring systems  have larger Δ_1 values than the five-membered ring systems , although the five-membered ring complex $Ni(dto)_2^{2-}$ exhibits the largest Δ_1 of the entire group.

TABLE IV

THE VALUE OF Δ_1 IN SOME PLANAR MS_4 COMPLEXES

$F_2 = 10F_4 = 800$ cm.$^{-1}$ for Ni(II)

$F_2 = 10F_4 = 600$ cm.$^{-1}$ for Pd(II) and Pt(II)

Complex[a]	Δ_1, cm.$^{-1}$	Complex[a]	Δ_1, cm.$^{-1}$
$Ni(mnt)_2^{2-}$	14,490[b]	$Pd(mnt)_2^{2-}$	17,800[b]
$Ni(mnt)_2^-$	15,200[b]	$Pd[S_2C_2(CF_3)_2]_2^{2-}$	19,050[c]
$Ni[S_2C_2(CF_3)_2]_2^{2-}$	15,700[c]	$Pd(SCN)_4^{2-}$	22,100[g]
$Ni(dtp)_2$	17,300[d]	$Pd(dtp)_2$	23,900[d]
$Ni(exan)_2$	18,300[d]	$Pd(dtc)_2$	24,300[d]
$Ni(dtc)_2$	18,600[d]	$Pd(dto)_2^{2-}$	28,100
$Ni(dmp)_2^{2-}$	19,000[e]	$Pt(mnt)_2^{2-}$	20,600[b]
$Ni(dtm)_2^{2-}$	20,200[f]	$Pt(dtp)_2$	25,900[d]
$Ni(dto)_2^{2-}$	20,500	$Pt(dto)_2^{2-}$	32,100

[a] Abbreviations used in the table: $mnt^{2-} = S_2C_2(CN)_2^{2-}$ = maleonitriledithiolate; $dtp^- = S_2P(OC_2H_5)_2^-$ = diethyl dithiophosphate; $exan^- = C_2H_5OCS_2^-$ = ethyl xanthate; $dtc^- = S_2NC(C_2H_5)_2^-$ = diethyl dithiocarbamate; $dmp^{2-} = S_2C_5H_5OH^{2-}$ = 2,3 dimercaptopropanol anion; $dtm^{2-} = S_2C_3H_2O_2^{2-}$ = dithiomalonate; $dto^{2-} = S_2C_2O_2^{2-}$ = dithiooxalate. [b] From ref. 5. [c] Spectrum from A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964). [d] Spectrum from C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962). [e] Spectrum quoted by D. L. Leussing, *J. Am. Chem. Soc.*, **81**, 4208 (1959). [f] Spectrum from W. A. Deskin, *ibid.*, **80**, 5680 (1958). [g] Spectrum from ref. 9, p. 287.

From the limited data available, it appears that the PdS_4 and PtS_4 series will be the same as the NiS_4 series. Furthermore, comparing complexes containing the same ligand we have the Δ_1 order Pt(II) > Pd(II) > Ni(II) for all the cases set out in Table IV.

It is interesting to compare the ligand-field splittings in the planar sulfur-donor metal complexes with the general Pt(II) planar spectrochemical series suggested by Chatt, Gamlen, and Orgel.[11] The Pt(II) series is (we have added I^-, Br^-, and Cl^-): $I^- < Br^- < Cl^- < R_2Te < R_2Se < R_2S < R_3As <$ piperidine $< R_3P < (RO)_3P$. Although the estimates are approximate, the PtS_4 Δ_1 values in Table IV indicate that mnt^{2-} and I^- are at nearly the same position, dtp^- is between R_2Te and R_2Se, and dto^{2-} is between R_2Se and R_3As. This comparison nicely illustrates the remarkable variability of the spectrochemical position of the planar MS_4 group.

Acknowledgments.—The authors gratefully acknowledge assistance with the computing provided by Mr. James Halper. We thank the National Science Foundation and the Rockefeller Institute for support of this research.

[11] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 468 (1958).