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Electronic Spectrum of Dichlorobis[*o*-phenylenebis(dimethylphosphine)]nickel(III) Hexafluorophosphate

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This report presents the polarized optical spectrum of a d^7 nickel(III) complex, $[Ni(dp)_2Cl_2]PF_6$, where dp is *o*-phenylenebis(dimethylphosphine), at 19 and 298 K and its interpretation based on electron repulsion calculations. Four crystal field transitions were observed centered at 15 260, 21 640, 23 650, and 24 800 cm^{-1}. The d-orbital ordering is assumed to be similar to that of $[Co(vpp)_2X]^+$ complexes, and where vpp is *cis*-1,2-bis(diphenylphosphino)ethylene and X = Cl, Br, and I. The energy level ordering based on the electron repulsion calculations is given by $xy > z^2 > xz > yz > x^2 - y^2$. This is further supported by a WHMO calculation.

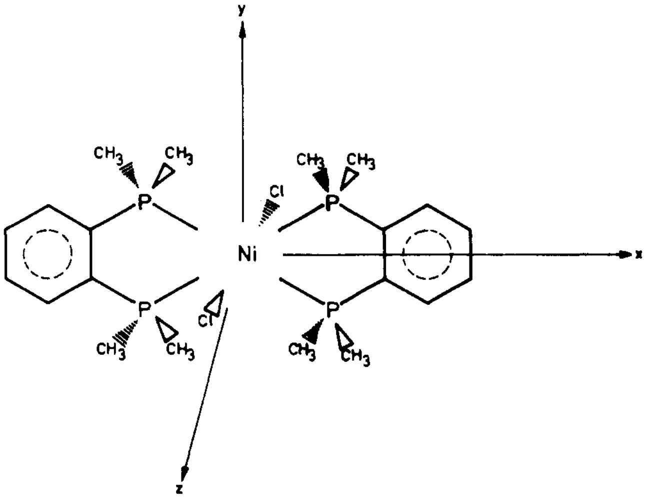
A number of ligands are known to form transition-metal complexes accompanied by the stabilization of unusual oxidation states of metal ions.[1-15] However, the bidentate bis(tertiary arsines) and bis(tertiary phosphines) could stabilize higher oxidation states of nickel only in the presence of some axial ligands like halides and hence form six-coordinated systems.[16-21] It had been suggested by Steifel et al.[12] that $[NiL_2]^-$ type of complexes where L is a bidentate dithiolene had a Ni(II)–radical ligand type of bonding rather than nickel being present in its formal oxidation state +3, whereas Kreisman et al.[13] proposed later a σ-stabilized radical ligand structure for $[Ni(diars)_2Cl_2]Cl$, where (diars) is *o*-phenylenebis(dimethylarsine). Interestingly enough, series of single-crystal EPR studies on complexes of this type[16-21] revealed the extensive delocalization of unpaired electron on ligands due to strong σ- and π-bond formation. However, the detailed analysis of the magnetic properties is hampered by the lack of optical data of single crystals. Hence we are presenting here the polarized optical spectral data of single crystals at 19 and 298 K and the assignments of the spectral transitions of $[Ni(dp)_2Cl_2]PF_6$, where (dp) is *o*-phenylenebis(dimethylphosphine).

Table I. Electronic Spectrum of $[Ni(dp)_2Cl_2]PF_6$, Relative Peak Heights Parallel and Perpendicular to the Molecular *z* Axis,[a] and Relative Oscillator Strengths at 19 and 298 K

band max, cm^{-1}	peak height at 19 K		oscillator strength[c]	
	parallel	perpendicular	19 K	298 K
15 260	0.72	1.38	32	33
21 640	0.6	1.70	45	69
23 650	3.60	0.50	12	16
24 800	0.50	4.00	120	172
28 420	*b*	*b*	154	253

[a] Since the bands at two different polarizations are being compared with the same full width at half-maximum, the heights are proportional to the intensities. Peak heights are transformed to molecular coordinates from experimental values. [b] It is difficult to measure its polarization due to the overlap of large intensity bands at high energy. [c] Oscillator strengths for experimental spectrum in perpendicular polarization.

The crystal belongs to the space group $P2_1/c$ with two molecules per unit cell.[22] The cation I contains four phosphorus atoms surrounding nickel in the equatorial plane and two chlorine atoms in axial position, with the bond lengths of Ni–P and Ni–Cl being 2.255 and 2.424 Å, respectively. This fragment has approximately D_{2h} symmetry. The *z* axes (Cl–Ni–Cl) of both molecules are roughly perpendicular to the crystallographic *ab* plane and make an angle of 20° with the crystallographic *c* axis. The polarization measurements were made with the light incident on the *bc* plane with the electric vector parallel and perpendicular to *c* axis. In the latter orientation, the electric vector is also approximately perpendicular to the molecular axis.



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(1) Nyholm, R. S. *J. Chem. Soc.* **1950**, 2071.
(2) Dwyer, F. P.; Mellor, D. P. *Chelating Agents and Metal Chelates*; Academic: New York, 1964; p 129.
(3) Feltham, R. D.; Kasenally, A.; Nyholm, R. S. *J. Organomet. Chem.* **1967**, *7*, 285.
(4) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.
(5) Feltham, R. D.; Silverthorn, W. *Inorg. Chem.* **1970**, *9*, 1207.
(6) Alyca, E. C. *Transition Metal Complexes of Phosphorous, Arsenic and Antimony Ligands*; McAuliffe, C. A., Ed.; MacMillan: London, 1973.
(7) Orton, J. W.; Auzins, P.; Griffiths, J. H. E.; Wertz, J. E. *Proc. Phys. Soc., London* **1961**, *78*, 554.
(8) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227.
(9) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1963**, *85*, 2029.
(10) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.
(11) Maki, A. H.; Berry, T. E.; Davison, A.; Holm, R. H.; Balch, A. L. *J. Am.* Chem. *Soc.* **1966**, *88*, 1080.
(12) Steifel, E. I.; Waters, J. H.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3016.
(13) Kreisman, P.; Marsh, R. E.; Preer, J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 1067.
(14) Nishida, Y.; Kida, S. *Coord. Chem. Rev.* **1979**, *27*, 275.
(15) Horrocks, W. D., Jr.; van Hecke, G. R.; Hall, D. D. *Inorg. Chem.* **1967**, *6*, 694.
(16) Manoharan, P. T.; Rogers, M. T. *J. Chem. Phys.* **1970**, *53*, 1682.
(17) Bernstein, P. K.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3035.
(18) Warren, L. F.; Bennet, M. A. *Inorg. Chem.* **1976**, *15*, 3126.
(19) Sethulakshmi, C. N.; Subramanian, S.; Bennett, M. A.; Manoharan, P. T. *Inorg. Chem.* **1979**, *18*, 2520.
(20) Sethulakshmi, C. N.; Manoharan, P. T. *Inorg. Chem.* **1981**, *20*, 2533.
(21) Balasivasubramanian, E.; Sethulakshmi, C. N.; Manoharan, P. T. *Inorg. Chem.* **1982**, *21*, 1684.
(22) Mahadevan, C.; Seshasayee, M.; Ramakrishna, B. L.; Manoharan, P. T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 38.

0020-1669/87/1326-3291$01.50/0

Table II. Assignments of Transitions of $[Ni(dp)_2Cl_2]^+$ and a Comparison with the Spectrum of $[Co(vpp)_2Cl]^+$

					$[Ni(dp)_2Cl_2]^+$			
					transition energy,[c] cm^{-1}			
1e transition	hole confign	state	$\epsilon_k([Ni(dp)_2Cl_2]^+)$,[a] cm^{-1}	interelectronic[b] repulsion energy	calcd	obsd	exptl polzn and enabling vibr species	$[Co(vpp)_2Cl]^+$ transition energy obsd, cm^{-1}
ground state	$(xy)^2(z^2)^1$	^2A_g	15 260	$3F_0 - 8F_2 + 33F_4$				
$z^2 \rightarrow xy$	$(xy)^1(z^2)^2$	$^2B_{1g}$	30 520	$3F_0 - 8F_2 + 33F_4$	15 260	15 260	$\perp$, B_{2u}, B_{3u}	13 450
$xz \rightarrow z^2$	$(xy)^2(xz)^1$	$^2B_{2g}$	~21 650	$3F_0 - 3F_2 + 8F_4$	~9 390	*e*	$\parallel$, A_u	7 170
$yz \rightarrow z^2$	$(xy)^2(yz)^1$	$^2B_{3g}$	23 590	$3F_0 - 3F_2 + 8F_4$	11 330	*e*		11 010
$x^2 - y^2 \rightarrow z^2$	$(xy)^2(x^2 - y^2)^1$	^2A_g	25 480	$3F_0 + 12F_2 - 67F_4$	22 220	23 650	$\parallel$, B_{1u}	23 470
$xz \rightarrow xy$	$(xy)^1(z^2)^1(xz)^1$	$^4B_{3g}$	36 910	$3F_0 - 12F_2 - 87F_4$	*d*	*d*		
		$^2B_{3g}{}^{(1)}$		$3F_0 - 6F_2 - 12F_4$	19 700			14 850
		$^2B_{3g}{}^{(2)}$		$3F_0 - 2F_2 - 32F_4$	21 100	21 640	$\perp$, A_u, B_{1u}	
$yz \rightarrow xy$	$(xy)^1(z^2)^1(xz)^1$	$^4B_{2g}$	38 850	$3F_0 - 12F_2 - 87F_4$	*d*	*d*		
		$^2B_{2g}{}^{(1)}$		$3F_0 - 6F_2 - 12F_4$	21 640	21 640	$\perp$, B_{1u}, A_u	19 810
		$^2B_{2g}{}^{(2)}$		$3F_0 - 2F_2 - 32F_4$	23 040	23 650	$\parallel$, B_{1u}	23 470
$x^2 - y^2 \rightarrow xy$	$(xy)^1(z^2)^1$ $(x^2 - y^2)^1$	$^4B_{1g}$	40 740	$3F_0 - 12F_2 - 87F_4$	*d*	*d*		
		$^2B_{1g}{}^{(1)}$		$3F_0 - 6F_2 - 12F_4$	23 530	23 650	$\parallel$, B_{1u}	23 470
		$^2B_{1g}{}^{(2)}$		$3F_0 - 2F_2 - 32F_4$	24 930	24 800	$\perp$, B_{2u}, B_{3u}	

[a] Sum of single-electron vacancy energies. [b] $F_2 = 1050$ cm^{-1}, $F_4 = 90$ cm^{-1} (based on 75% of the free ion value). [c] Sum of single-electron vacancy enegies and electron repulsion energy minus the ground-state total energy. [d] Spin forbidden. [e] Inability to measure these bands due to limited spectrometer range.

The electronic spectrum of the title complex in acetonitrile solution in the region 10000–40000 cm^{-1} measured with a Carl-Zeiss DMR-21 spectrophotometer is shown in Figure 1. Polarized optical spectra in the region 14300–27000 cm^{-1} at 19 and 298 K, which were measured with a microspectrophotometer developed in this laboratory,[23] are shown in Figure 2. These spectra are fitted to five bands centered at 15260, 21640, 23650, 24800, and 28420 cm^{-1} by using standard computer programs.[24] Comparison of peak heights in parallel and perpendicular polarizations at 19 K and oscillator strengths at 19 and 298 K at parallel orientation are given in Table I. The first four bands reveal a decrease in intensity as the temperature is lowered from 298 to 19 K, indicating their orbital forbidden nature.

In general, the electronic spectrum of $[Ni(dp)_2Cl_2]^+$ seems to be quite similar to that of $[Co(vpp)_2X]^+$ type of compounds (where vpp is *cis*-1,2-bis(diphenylphosphino)ethylene) whose electronic spectrum has been analyzed in detail.[15,20] However, there is one difference between these two systems. The overall d-orbital splitting in $[Ni(dp)_2Cl_2]^+$ should be definitely larger than that in $[Co(vpp)_2X]^+$ because of a higher nuclear charge (+3) in nickel and the presence of an extra ligand in the axial position. Keeping in mind the earlier spectral assignments of $[Co(vpp)_2Cl]^+$ and the present polarization data, we have attempted to assign the various electronic transitions in $[Ni(dp)_2Cl_2]^+$. The intensity ratios of the parallel and perpendicular spectra indicate the presence of both parallel and perpendicular components in all the bands though one of the polarizations always dominates. Any possible shifts in peak positions due to molecular/lattice contractions are ruled out on the basis of an earlier ESR work on these crystals in the region 77–298 K.[25] Since all these transitions are parity forbidden due to D_{2h} symmetry of the complex ion, these electric dipole allowed transitions must attain intensity by a vibronic mechanism involving one or more enabling vibrations. Assuming the d-orbital

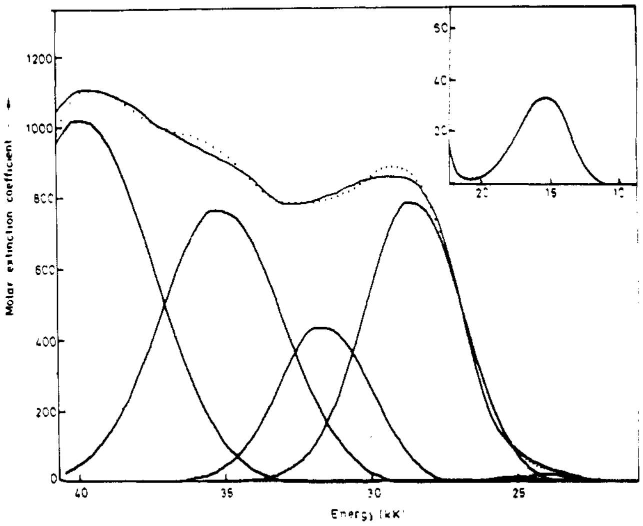

Figure 1. Electronic spectrum of $[Ni(dp)_2Cl_2]PF_6$ observed (···) and deconvoluted showing the fitting (–) in acetonitrile solution. Insert shows the spectrum in the region 10–20 × 10^3 cm^{-1}.

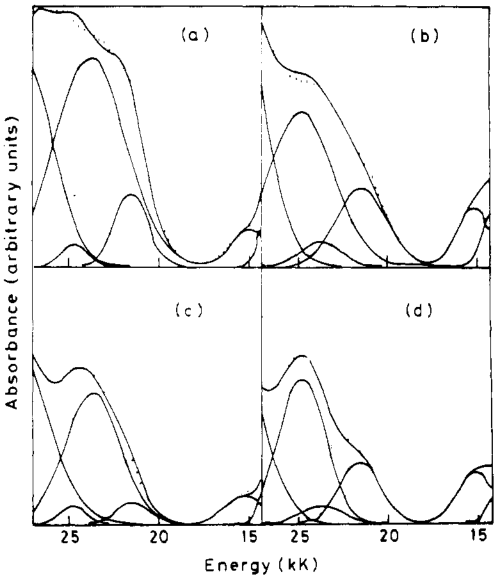

Figure 2. Electronic spectrum of $[Ni(dp)_2Cl_2]PF_6$ observed (···) and deconvoluted showing the fitting (–) for the electric vector in the *bc* plane: (a) parallel to the *c* axis at 298 K; (b) perpendicular to the *c* axis at 298 K; (c) parallel to the *c* axis at 19 K (d) perpendicular to *c* axis at 19 K.

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(23) The microspectrophotometer was designed for the absorption spectral measurements in the region 200–700 nm of small crystals of area 0.5 × 0.5 mm^2. It is a single-beam instrument in which all the optical components are mounted on a rail that is fixed on an optical table. The source is a 150-W xenon arc lamp. An Oriel 7240 model monochromator with an Oriel 7270 reflection grating is used. The beam is polarized with a Glan prism and focused on the crystal by using a condensing lens system. The crystal mount is fixed to the cold head of a CTI Cryogenics cryodyne cryocooler. The beam that is transmitted through the crystal is focused on an EMI 6256A photon-counting photomultiplier tube and the signal is recorded on a printer. The reliability of absorbance measured is ±0.002. The resolution used to record the spectra presented here is about 3.0 nm.

(24) (a) Barker, B. E.; Fox, M. F. *Chem. Soc. Rev.* **1980**, *9*, 143. (b) A deconvolution program was kindly supplied by Dr. G. L. Burkhart, Department of Chemistry, University of Nevada; it was suitably modified to run on a computer with BASIC language facility.

(25) Ramakrishna, B. L. Ph.D. Thesis.

ordering[17,19,20] of $xy > z^2 > xz > yz > x^2 - y^2$ the ground state ^2A_g has the hole configuration $(xy)^2(z^2)^1$. Under D_{2h} symmetry, $z^2(a_g)$ and $x^2 - y^2(a_g)$ will mix and the admixture seems to be small as revealed by very small orthorombicity in the ESR spin-Hamiltonian parameters.[19] All the excitations must be spin allowed. Spin-allowed transitions can be obtained by promoting electrons from z^2 to xy and from the filled d levels to the half-filled z^2 orbital or to the empty xy orbital. The one-electron transitions, vacancy configurations, the spectroscopic ground and excited states, and the interelectronic repulsion energies associated with them are listed in Table II. From Table II it is clear that the first band at 15 260 cm^{-1} can be unequivocally assigned to $^2A_g \rightarrow {}^2B_{1g}$ ($z^2 \rightarrow xy$) with an enabling vibration B_{2u} and/or B_{3u}. This assignment accounts for perpendicular polarization. However, a small admixture with an enabling vibration A_u cannot be ruled out, which would give this transition parallel polarization. Similarly, the band at 21 640 cm^{-1} can be a combination band from $^2A_g \rightarrow {}^2B_{3g}{}^{(2)}$ and $^2A_g \rightarrow {}^2B_{2g}{}^{(1)}$ resulting from the excitations $xz \rightarrow xy$ and $yz \rightarrow xy$, and the large intensity band at 23 650 cm^{-1} can be a combination of up to three different bands $^2A_g \rightarrow {}^2A_g$ ($x^2 - y^2 \rightarrow z^2$), $^2A_g \rightarrow {}^2B_{2g}{}^{(2)}$ ($yz \rightarrow xy$), and $^2A_g \rightarrow {}^2B_{1g}{}^{(2)}$ ($x^2 - y^2 \rightarrow xy$), since these bands are all mainly parallel polarized. Finally the band at 24,800 cm^{-1} can be assigned to $^2A_g \rightarrow {}^2B_{1g}{}^{(2)}$ ($x^2 - y^2 \rightarrow xy$). The entire assignment and justification for polarizations are given in Table II. The band observed at 28 420 cm^{-1} should be of ligand → metal origin.

A calculation using the Wolfsberg–Helmholz molecular orbital method was performed with the valence orbitals of ligands and metal as the basis functions. The energy level ordering obtained is $xy > z^2 > yz + L \sim xy + L > x^2 - y^2 > yz \sim xz$. The d orbitals appearing above and below $x^2 - y^2$ with varying amounts of admixture simply suggest the delocalized nature of the electrons in these orbitals. We presume that the WHMO calculation has underestimated the d–orbital populations in the molecular orbitals appearing above $x^2 - y^2$. It is, however, interesting to note that the ordering of the levels and the ground state predicted by WHMO calculation is consistent with our spectral assignments.

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Electron Spin Resonance Investigation of Copper(I)–9,10-Phenanthrenesemiquinonate Complexes

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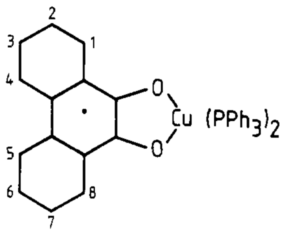
Electron spin resonance spectra of copper(I) complexes with the structures of $[CuL_2(SQ)]$ and $[CuL(SQ)]$ have been investigated in different solvents, where SQ is substituted 9,10-phenanthrenesemiquinonate and L is triphenylphosphine. The well-resolved hyperfine patterns of ^{63}Cu, ^{65}Cu, ^{31}P, and protons of SQ were analyzed by computer simulations. The spectral parameters of mono complexes in coordinating solvents were found intermediate between the data of mono- and bis(phosphine) complexes in noncoordinating solvents. The spin densities on the Cu and P atoms and SQ ring were found to vary oppositely, which could be expected from the electron affinity and half-wave potential of SQ. This anomaly was explained by a three-electron bonding scheme between one filled 3d orbital of copper and the delocalized π-system of SQ, which suggests opposite direction of the spin and charge transport between the metal ion and SQ.

Introduction

The electron spin resonance (ESR) spectra of various (*o*-semiquinonato)copper(I) complexes with neutral ligands have been investigated by Razuvaev et al.[1] They classified these complexes as radicals since the unpaired electron is mainly localized on the *o*-semiquinonate ligands (SQ). There is, however, a small fraction of spin density on the central ion and the neutral ligands (L) too, which yields hyperfine splitting due to the couplings of ^{63}Cu, ^{65}Cu, and ^{31}P nuclei. These couplings were found to depend sensitively on the coordination number of copper ion: for complexes [CuL(SQ)] with trigonal geometry small splittings were observed, while for the complexes $[CuL_2(SQ)]$ with tetrahedral geometry large splittings were observed. In the latter case the couplings of ^{63}Cu, ^{65}Cu, and ^{31}P nuclei vary anomalously with the electron affinity of SQ: the larger the electron affinity, the larger the spin density that can be observed on the metal ion and neutral ligand.

In order to obtain further details of the spin distribution in complexes with the structure $[CuL_n(SQ)]$ ($n = 1$ or 2), we studied substituted copper(I)–9,10–phenanthrenesemiquinonate complexes with the neutral ligand triphenylphosphine.



Since the *o*-semiquinone ligand possesses a large delocalized π-electron system, not only can we study the variation of spin densities on the metal ion and neutral ligands but information can also be obtained from the rearrangement of spin distribution on SQ, when different substituents are applied.

Experimental Section

All reactions were carried out under an atmosphere of pure, dry argon with the use of standard Schlenk-type glassware and techniques. 9,10-Phenanthrenequinone (Fluka), triphenylphosphine (Fluka), and copper powder (Reanal) were used as supplied. 1-Nitro-9,10-phenanthrenequinone,[2] 2-nitro-9,10-phenanthrenequinone,[3] 3-nitro-9,10-

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(1) Razuvaev, G. V.; Cherkasov, V. K.; Abakumov, G. A. *J. Organomet. Chem.* **1978**, *160*, 361.
(2) Dewar, M. J. S.; Warford, E. W. T. *J. Chem. Soc.* **1956**, 3570.