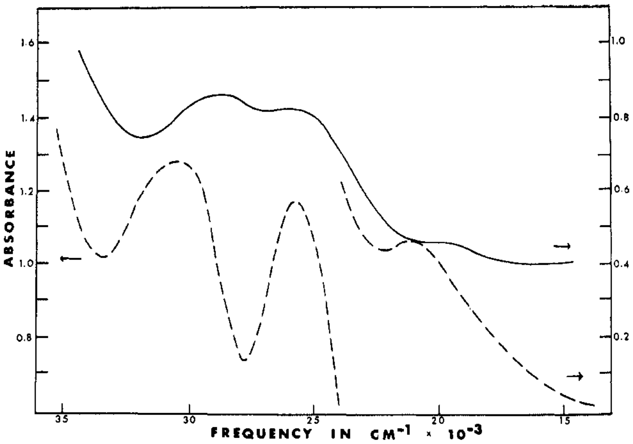

Figure 1.—Spectra of K_2PtCl_4: ----, 12 *N* HCl; ———, LiCl–KCl eutectic, 400°.

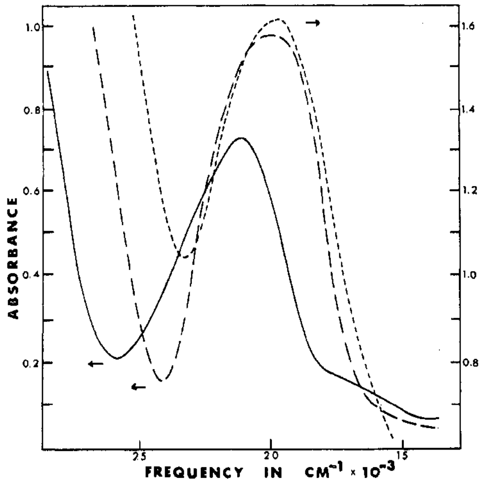

Figure 2.—Spectra of Cs_2PdCl_4: ———, 6 *N* HCl; ----, LiCl–KCl eutectic, 400°; --------, LiCl–KCl eutectic, 600°.

TABLE I

SPECTRA OF K_2PtCl_4 AND Cs_2PdCl_4 IN VARIOUS SOLVENTS

	Band maxima, cm^{-1} (ϵ_{max})		
Solution	$^1A_{1g} \rightarrow {}^3E_g$	$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1E_g$
K_2PtCl_4 in 12 *N* HCl	21,200 (22)	25,700 (57)	30,400 (65)
K_2PtCl_4 in H_2O	21,100 (18)	25,600 (60)	30,500 (69)
K_2PtCl_4 in LiCl–KCl eutectic, 400°	19,500 (~8)	25,600 (~15)	28,800 (~15)
K_2PtCl_4 in LiCl–KCl eutectic, 450°	19,000 (~8)	25,600 (~15)	28,400 (~15)
Cs_2PdCl_4 in 6 *N* HCl		21,200 (150)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 400°		20,300 (~240)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 500°		20,100 (~260)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 600°		19,900 (~270)	

The first possibility can be eliminated as the primary cause of the spectral changes in this example by a consideration of the shifts of the bands as observed by Martin, *et al.*,[7] in their investigation of the polarized crystal spectra of K_2PtCl_4 at 15 and 298°K. These workers found that the shifts of the three bands ($^1A_{1g} \rightarrow {}^3E_g$, $^1A_{2g}$, ^1E_g) were all of about the same magnitude. It is obvious from Figure 1 that this is not the case here, so that some other effect must also be considered.

Distortion to a tetrahedral structure is unlikely since the changes in the spectrum are comparatively slight. Gruen and McBeth,[11] in their study of Ni(II) in chloride melts, found a tetrahedral configuration in CsCl, but a tetragonal structure in LiCl. The larger size of Pt(II) would tend to favor the latter, while the chemical properties of this species make a tetrahedral form unexpected. Possibility c is more attractive from the latter point of view and can be justified from the nature of the spectral changes.

The orientation of solvent anions above and below the molecular plane will destabilize the d_{z^2} and d_{xz}, d_{yz} orbitals relative to the $d_{x^2-y^2}$ and d_{xy} orbitals, while not affecting the energy separation between the latter pair. Thus the $^1A_{1g} \rightarrow {}^1A_{2g}$ band should not shift, while the $^1A_{1g} \rightarrow {}^3E_g$, ^1E_g bands should shift toward the red, as is observed. A similar shift was observed and interpreted in the same way by Chatt, *et al.*,[3] for $[\{(n\text{-}C_5H_{11})_2NH\}_2PtCl_2]$ in hexane and ethanol. The fact that the bands shift further toward the red on increasing the temperature follows from the observation by Hafner and Nachtrieb in their nmr studies of molten salts[12] that cations and anions associate in molten salts with a positive temperature coefficient. If this holds for the melt chloride ion–platinum interactions here, the d_{z^2} and d_{xz}, d_{yz} orbitals would be further raised relative to the d_{xy} and $d_{x^2-y^2}$ orbitals.

Although the same arguments will hold for $[PdCl_4]^{2-}$, the situation is not so well defined since the observed band is actually a composite of the bands due to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g. However, it is observed that on going to the LiCl–KCl eutectic the band becomes more symmetrical, indicating that the $^1A_{1g} \rightarrow {}^1E_g$ is shifting toward the red.

[11] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

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Nickel(II) Complexes of Aromatic Amine Oximes

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Complexes utilizing *s*-triazines as ligands have not been extensively investigated. It would be of interest to see how such compounds compare with analogous pyridine ligands. For this reason we have prepared

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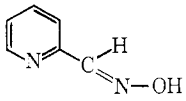
complexes of the type NiL_2X_2, where L is 2-pyridinaldoxime (**1**, HPOX), 6-methyl-2-pyridinaldoxime (**2**, HMPX), and 4,6-dimethyl-*s*-triazine-2-aldoxime (**3**, HTzX). Nickel(II) complexes of **1** have been investigated;[2] since the 6-methyl group in ligand **3** should exhibit some effect on its complexes we also studied the complexes of ligand **2**, containing such a function. These compounds are discussed below.



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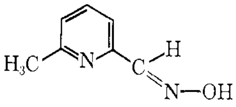

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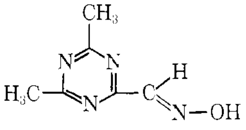

3

Experimental Section

Reagents.—2-Pyridinaldoxime (HPOX) and 6-methyl-2-pyridinaldoxime (HMPX) were obtained from Aldrich Chemical Co. 2,4,6-Trimethyl-*s*-triazine was synthesized according to the method of Schaefer and Peters;[3] this compound was used to prepare 4,6-dimethyl-*s*-triazine-2-aldoxime by the method of Grundmann and Mini.[4] Nickel(II) chloride hexahydrate was reagent grade; nickel(II) bromide was prepared from nickel(II) carbonate and hydrobromic acid, the hydrate crystallizing on evaporation of the resulting solution.

Complexes.—$[Ni(HTzX)_2Br_2]$ was prepared by mixing the components in boiling acetone–water, sufficient water being added to obtain one liquid phase. The product crystallized on standing. Other complexes of the $[NiL_2X_2]$ type were prepared by dissolving the components in hot 95% ethanol and mixing. $Ni(HPOX)_3I_2 \cdot 2H_2O$ was prepared as described earlier.[2] All compounds were dried *in vacuo* over phosphoric anhydride.

Magnetic Moments.—The Gouy method was employed to determine magnetic susceptibilities at room temperature; $HgCo(SCN)_4$ was used to standardize the apparatus.[5] Measurements, made at two different field strengths, indicated the absence of ferromagnetic impurities. Magnetic susceptibilities were calculated assuming the validity of the Curie law (*i.e.*, a negligible Weiss constant). Pascal's constants were used to calculate the diamagnetic susceptibilities of ligands **1**, **2**, and **3**; standard values for the diamagnetic corrections for other ions were used.[5]

Electronic Spectra.—Mineral oil mulls sandwiched between quartz plates were run on a Cary Model 14 spectrophotometer. Neutral density filters were placed in the reference beam. Spectra were recorded from 10,500 to 3000 A.

Calculations assuming O_h symmetry used the energies

$$E(^3A_{2g}) = -12Dq \qquad E(^3T_{2g}) = -2Dq$$

$$E(^3T_{1g},F) \text{ and } E(^3T_{2g},P) \quad \begin{vmatrix} 8Dq + 3B - E & 6B \\ 6B & -2Dq + 12B - E \end{vmatrix} = 0$$

Analyses.—Compounds were analyzed by G. I. Robertson (Florham Park, N. J.) and by Galbraith Laboratories (Knoxville, Tenn.).

Results and Discussion

In Table I are listed the compounds under consideration in this study, together with their analyses, room-temperature magnetic susceptibilities, and magnetic moments. Electronic spectral data are compiled in Table II; these data were all obtained by transmission through mineral oil mulls. Since the compounds dissociate in solution (to form electrolytes) solution spectra were not studied. Table III contains a summary of the crystal field parameters derived from the electronic spectral data.

We were unable to isolate a tris complex of HMPX. The steric effect of a methyl group in the 6 position could be responsible for our inability to isolate $Ni(HMPX)_3^{2+}$. Much data on complexes of substituted dipyridyl type ligands[6] indicate the possibility of a steric effect in these compounds. However, a large excess of HMPX in hot solution causes the brown color of what may be a tris complex to predominate; on cooling, excess ligand crystallizes. The presumed low stability of $Ni(HMPX)_3^{2+}$ may simply be due to insolubility of the ligand.

The magnetic moments of these complexes are those generally observed for octahedral nickel(II), being approximately 3.1 BM. Any distortions from O_h (see below) are not sufficient to produce a singlet ground state; nor is the distortion such as to cause an increase in the magnetic moment as proposed by Lever.[7]

A study of the electronic spectra of these compounds shows a significant difference from typical O_h complexes in that the lowest energy band (in the 10,000 cm^{-1} region) is split into two peaks. If we temporarily assume O_h symmetry for these compounds, assign the higher energy of these two lower peaks as the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, and assign the band in the 17,000 cm^{-1} region as the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition we can then calculate the Racah parameter B and the energy of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition. Reference to Table III, in which crystal field parameters are summarized, shows the agreement between calculated and observed values for this transition to be poor. This, plus the splitting of the first band, suggests the compounds to be of lower symmetry than O_h, probably D_{4h}.

Several workers have considered nickel(II) complexes in noncubic fields. Recently Karn and Busch[8] have used the crystal field model in considering electronic spectra of D_{4h} nickel(II) complexes. This model utilizes, in addition to Dq, the two parameters Ds and Dt, related to the axial distortion from cubic symmetry. In the D_{4h} representation the ground state ($^3B_{1g}$) is raised $7Dt$ above the O_h ground term ($^3A_{2g}$). The first excited state ($^3T_{2g}$ in O_h) is split into two components, a $^3B_{2g}$ (raised $7Dt$ above the original $^3T_{2g}$) and a lower ^3E_g. Between these two states there is a total separation of $^{35}/_4Dt$. Thus, the first allowed transition is equal to $10Dq - {}^{35}/_4Dt$ and the second defines Dq. Splitting in the higher states is generally not observed and consequently Ds cannot be evaluated.

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(2) R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960).

(3) F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961).

(4) C. Grundmann and V. Mini, *ibid.*, **29**, 678 (1964).

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(7) A. B. P. Lever, *Inorg. Chem.*, **4**, 763 (1965).

(8) J. L. Karn and D. H. Busch, paper presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

TABLE I

ANALYSES AND MAGNETIC DATA FOR COMPLEXES

Compd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	N, % Found	N, % Calcd	Halogen, % Found	Halogen, % Calcd	$\chi_M \times 10^6$ obsd	$\chi_{Ni} \times 10^6$ (cor)	T, °K	μ_{eff}, BM
$Ni(HPOX)_2Cl_2$	38.15	38.5	3.31	3.23	14.90	15.0	18.64	19.0	3941	4106	296	3.11
$Ni(HPOX)_2Br_2$	31.44	31.1	2.77	2.61	12.06	12.1	33.85	34.5	3536	3723	296	2.97
$Ni(HMPX)_2Cl_2$	41.94	41.8	4.09	4.52	14.01	14.0	17.50	17.6	4107	4196	296	3.19
$Ni(HMPX)_2Br_2$	34.16	34.3	3.29	3.29	11.27	11.4	33.41	32.5	4063	4274	296	3.18
$Ni(HTzX)_2Cl_2$	33.09	33.2	3.85	3.71	25.61	25.8	16.15	16.3	3874	4070	293	3.09
$Ni(HTzX)_2Br_2$	27.55	27.6	3.24	3.08	21.50	21.5	30.61	30.5	4054	4272	296	3.18

TABLE II

ELECTRONIC SPECTRAL DATA EOR COMPLEXES STUDIED (CM^{-1})[a]

$Ni(HPOX)_2Cl_2$	$Ni(HPOX)_2Br_2$	$Ni(HMPX)_2Cl_2$	$Ni(HMPX)_2Br_2$	$Ni(HTzX)_2Cl_2$	$Ni(HTzX)_2Br_2$	$Ni(HPOX)_3I_2$	Assignment (D_{4h})
						10,200 w	
10,200	10,200	10,100	9,820	10,200	10,100	11,800 sh	$^3B_{1g} \rightarrow {}^3E_g{}^a$
10,700	10,900 sh	10,500	10,400 sh	10,500	10,500	12,700	$^3B_{1g} \rightarrow {}^3B_{2g}$
12,200 sh	11,200 vb	12,200 sh	11,700 sh		11,800 sh	14,100 sh	$\}$ → singlets
13,200 w	12,200	13,300 sh	13,300 sh		13,300 sh		
16,950	17,600	17,100	16,300	17,200	16,800	19,200 sh	$^3B_{1g} \rightarrow {}^3A_{2g} + {}^3E_g{}^b$
28,200 sh	31,400	30,900	27,400 sh	32,600 sh	30,800	26,500	$\}$ $^3B_{1g} \rightarrow {}^3A_{2g} + {}^3E_g(P)$
31,200	32,000 sh	32,000					

[a] sh, shoulder; w, weak; vb, very broad.

TABLE III

CRYSTAL FIELD PARAMETERS (CM^{-1})

Compound	*Dq*(compound)	*Dq′* (aromatic ligand)	*Dt*	*B*	$^3T_{2g} \rightarrow {}^3T_{1g}(P)$ Calcd	$^3T_{2g} \rightarrow {}^3T_{1g}(P)$ Obsd
$Ni(HPOX)_2Cl_2$	1070	1240	56	815	27,300	28,200 or 31,200
$Ni(HPOX)_2Br_2$	1090	1280	74	971	29,500	31,400
$Ni(HMPX)_2Cl_2$	1050	1220	45	948	28,600	30,900
$Ni(HMPX)_2Br_2$	1040	1210	68	732	25,900	27,400
$Ni(HTzX)_2Cl_2$	1050	1220	40	1003	29,300	32,600
$Ni(HTzX)_2Br_2$	1050	1220	47	825	29,000	30,800
$Ni(HPOX)_3I_2$	1270	1270	107	730	29,900	26,500

Unfortunately, this method does not allow us to calculate the position of the components of the $^3T_{1g}(P)$ state and thereby check the parameters.

Table III contains values of *Dt* determined from the spectra using the above relationships. The small values for *Dt* imply a small distortion from O_h; consequently the *B* values, calculated assuming a cubic model, are probably not excessively in error. Because of this small distortion from O_h it is difficult to rationalize the discrepancy between the observed and calculated values for the O_h transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$.

Examination of the *B* values given in Table III points out an interesting anomaly. For HMPX and HTzX complexes $B_{Br^-} < B_{Cl^-}$. One expects this since the nephelauxetic effect of bromide is greater than that of chloride.[9] Just the opposite effect is observed in the HPOX complexes. This could be ascribed to varying degrees of π bonding in the two groups of compounds. In this context it is interesting to consider a paper by Lever, Nelson, and Shepherd.[10] In a study of the electronic spectra of some nickel(II) halide amine complexes these workers proposed that the ratio Dq'_{Br}/Dq'_{Cl} (where Dq' is the Dq value of the amine ligand in the complex calculated using average environment) could be used to indicate the presence of π bonding in metal–ligand bonds. Ratios greater than unity indicate such an interaction. We have calculated these ratios for our compounds and find them to be unity. If the postulate of Lever, *et al.*, is correct, and it appears to be logical, we may assume π bonding in the compounds presently under discussion to be negligible. One must seek elsewhere for an answer to the *B* value discrepancy we have noted above; at present it remains unexplained.

The *Dq′* values listed in Table III were calculated assuming the rule of "average environment" to hold. Considering the small *Dt* values this is probably a valid assumption. (For this purpose, values of 720 and 700 cm⁻¹ for *Dq* of the chloride and bromide ions were used.[9]) All three amine oximes give similar *Dq* values. Since HMPX and HTzX give identical values, it is safe to say that any differences between these ligands and HPOX are due to the methyl groups in the 6 position; the *s*-triazine ring system appears to be very similar in its donor properties (with nickel(II)) to the pyridine ring system. Further work with ligands derived from this ring system should prove fruitful.

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