Chemistry, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974; see Abstracts, No. INOR-64.

(2) Some recent reviews: (a) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968); (b) E. L. Muetterties, *ibid.*, **3**, 266 (1970); (c) K. Vrieze and P. W. N. M. Van Leeuwen, *Prog. Inorg. Chem.*, **14**, 1 (1970); (d) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem. Int. Ed. Engl.*, **9**, 703 (1970); (e) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971); (f) E. L. Muetterties, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 77 (1972); (g) J. P. Jesson and P. Meakin, *Acc. Chem. Res.*, **6**, 269 (1973); (h) J. R. Shapley and J. A. Osborn, *ibid.*, **6**, 305 (1973).

(3) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971).

(4) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).

(5) L. H. Pignolet and G. N. La Mar in "Chemical Applications of NMR in Paramagnetic Molecules", G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N.Y., 1973, Chapter 8.

(6) F. A. Cotton and L. M. Jackman, Ed., "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1975.

(7) J. G. Gordon, II, and R. H. Holm, *J. Am. Chem. Soc.*, **92**, 5319 (1970).

(8) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(9) E. L. Muetterties, "Stereochemistry", Cornell University Press, Ithaca, N.Y., 1974.

(10) M. Gielen and N. Van Lautem, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970).

(11) A. T. Balaban, *Rev. Roum. Chim.*, **18**, 841 (1973).

(12) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.*, **93**, 4701 (1971).

(13) W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

(14) W. G. Klemperer, *Inorg. Chem.*, **11**, 2668 (1972).

(15) W. G. Klemperer, *J. Am. Chem. Soc.*, **94**, 6940 (1972).

(16) W. G. Klemperer, *J. Am. Chem. Soc.*, **95**, 2105 (1973).

(17) J. I. Musher, *Inorg. Chem.*, **11**, 2335 (1972).

(18) J. I. Musher, *J. Chem. Educ.*, **51**, 94 (1974).

(19) J. I. Musher and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 1320 (1974).

(20) J. S. Miller and K. J. Caulton, *J. Am. Chem. Soc.*, **97**, 1065 (1975).

(21) P. Finocchiaro, *J. Am. Chem. Soc.*, **97**, 4443 (1975).

(22) W. Hasselbarth and E. Ruch, *Theor. Chim. Acta*, **29**, 259 (1973).

(23) D. J. Klein and A. H. Cowley, *J. Am. Chem. Soc.*, **97**, 1633 (1975).

(24) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **95**, 1825 (1973).

(25) An averaging set is comprised of all allowed permutations which generate the same net NMR site interchange pattern. A rearrangement mode[17,18] refers to a class of stereoisomerizations in which the relative orientation of a certain subset of all of the ligands changes. Where mirror-image symmetry is present in molecules, rearrangements have been classified in terms of "observable processes".

(26) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).

(27) N. Serpone and K. A. Hersh, *Inorg. Chem.*, **13**, 2901 (1974).

(28) N. Serpone and K. A. Hersh, *J. Organomet. Chem.*, **84**, 177 (1975).

(29) D. G. Bickley, M.Sc. Thesis, Concordia University, Montreal, 1975.

(30) N. Baggett, D. S. Poolton, and W. B. Jennings, *J. Chem. Soc. Chem. Commun.*, 239 (1975).

(31) R. C. Fay and A. F. Lindmark, *J. Am. Chem. Soc.*, **97**, 5928 (1975).

(32) For a partial description of the analysis of *cis*-$M(AA)_2XY$ complexes, see ref 24.

(33) D. G. Bickley and N. Serpone, *Inorg. Chem.*, **13**, 2908 (1974).

(34) Permutational isomers (or permutamers[35]) have been defined[2d] as "chemical compounds which have in common the same molecular skeleton and set of ligands, differing only by the distribution of the ligands on the skeletal positions".

(35) R. D. Adams and F. A. Cotton, *J. Am. Chem. Soc.*, **95**, 6589 (1973).

(36) For a more formal derivation of the set of all P and P^* of the ligating nuclei for a complex having configuration **2**, see footnote 9 of ref 24.

(37) Because this system possesses C_1 symmetry, it may be argued that there should be 16 nonequivalent permutations and therefore 16 averaging sets. The difference would seem to lie between the two random scrambling permutations (12)(56) and (34)(56) which cyclically permute terminal AA groups among all four environments but with the direction of the cycle being different in the two cases, viz., $a \rightarrow c \rightarrow b \rightarrow d$ and $a \leftarrow c \leftarrow b \leftarrow d$, respectively. Making an arbitrary assignment of the four CH_3 NMR signals in *cis*-$(CH_3)ClSn(acac)_2$[27] and employing a multisite exchange program (DNMR3, QCPE, University of Indiana) we[38] tested all six random-exchange matrices under the same conditions in the input parameters. We observed that four of the six matrices produced the same calculated methyl NMR spectra while the remaining two matrices yielded different (but mutually the same) spectra. Interestingly, the latter two random-exchange matrices never occur in all of the plausible mechanisms envisaged for the rearrangement processes. Thus, we[33] placed the (12)(56) and (34)(56) permutations within the same averaging set according to the definition of averaging sets,[25] to give 14 A_i' without precluding the possibility that each of these two permutations describes the subsets A_{6a}', A_{6b}', A_{13a}', and A_{13b}'.[39]

(38) K. A. Hersh, M.Sc. Thesis, Concordia University, Montreal, 1975.

(39) Averaging sets described earlier[33] were labeled differently. Averaging sets A_1 through A_7 are herein referred to as A_1' through A_7' while A_1' through A_7' are herein denoted A_8' through A_{14}'.

(40) Two other diastereomers exist which possess mutually trans X groups.

(41) Diastereomers are referred to by three cis or trans prefixes which specify the relative orientations of the X, R_1, and R_2 groups in that particular sequence.

(42) D. G. Bickley and N. Serpone, to be submitted for publication.

Contribution from the Department of Petroleum Chemistry,
Faculty of Engineering, Osaka University, Suita, 565 Japan

Additions of Alcohols to Simple Nitriles Coordinated to the Cationic Pentachlorophenylnickel(II) Moiety. Isolation of Imidate Complexes

MASANORI WADA* and TOSHIYUKI SHIMOHIGASHI

Received May 2, 1975 AIC50301B

Cationic pentachlorophenylnickel(II) complexes, *trans*-$[C_6Cl_5Ni(P)_2NCR]^+ClO_4^-$ (P = $PPhMe_2$, PPh_2Me; R = Me, CH_2Ph, Ph), **2**, prepared from *trans*-$C_6Cl_5Ni(P)_2Cl$, silver perchlorate, and nitriles in benzene were treated with methanol or ethanol in the presence of triethylamine, to yield the corresponding imidate complexes, *trans*-$[C_6Cl_5Ni(P)_2NH{=}C(R)OR']^+ClO_4^-$, **3**, identified by ir and ^1H NMR spectra and elemental analyses. The ^1H NMR spectra revealed the products obtained from **2** (P = $PPhMe_2$) to be mixtures of complexes **3** containing isomeric imidate groups. The major isomer (P = $PPhMe_2$, R = Ph, R' = Me) was shown by ^1H NMR spectroscopy to be the cis adduct. Complex **2** (P = $PPhMe_2$, R = Me) readily undergoes substitution of the acetonitrile ligand with Br^-, I^-, NCS^-, $OOCMe^-$, and $P(OMe)_3$.

Introduction

In recent years there has been considerable interest in addition of water or of alcohols to a nitrile multiple bond within the coordination sphere of metal ions.[1] The initial step is thought to involve nucleophilic attack of an external or coordinated hydroxide or alkoxide anion on the nitrile carbon atom. Such intermediate imidate complexes have been isolated from reactions of 2-cyanopyridine complexes,[2] of perfluorobenzonitrile complexes,[3] and of *o*-cyanobenzylplatinum complexes,[4] but few simple nitrile complexes seem to be known except for rhenium–acetonitrile complexes.[5] In connection with our current research program concerning the syntheses and reactions of cationic organonickel(II) complexes, we report here the synthesis of simple nitrile complexes and their reactions with alcohols in an attempt to isolate the corresponding imidate complexes.

Results and Discussion

Preparation of Nitrile Complexes, *trans*-$[C_6Cl_5Ni$-

Table I. Analytical Data for Nitrile-Nickel(II) Complexes, *trans*-$[C_6Cl_5Ni(P)_2NCR]^+ClO_4^-$

Complexes					% C		% H		% N	
No.	P	R	Yield, %	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
2a	$PPhMe_2$	CH_3	93	191–193	39.77	39.83	3.48	3.53	1.93	2.12
2b		$CH_2C_6H_5$	77	168–169	44.99	44.99	3.65	3.44	1.75	1.76
2c		C_6H_5	92	188–189	44.26	44.10	3.46	3.27	1.78	1.87
2d	PPh_2Me	CH_3	67	222–224	47.88	47.72	3.33	3.44	1.92	1.65
2e		$CH_2C_6H_5$	72	193–195	51.75	51.94	3.34	3.60	1.45	1.51
2f		C_6H_5	64	209–211	51.42	51.30	3.43	3.40	1.54	1.68

Table II. Spectral Data for Nitrile-Nickel Complexes

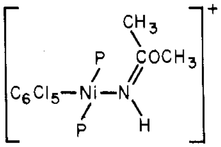
	Ir spectra, cm^{-1}				^1H NMR spectra			
Complex	$\nu(C{\equiv}N)^a$	$\Delta\nu(C{\equiv}N)^b$	$\nu(ClO_4^-)^c$	$\delta(ClO_4^-)^d$	Solvent	$\tau(P\text{–}CH_3)$,^{e} ppm	$\tau(R)$, ppm	Conductivity,^{f} Ω^{-1} cm^2
2a	2295	41	1090	625	$CDCl_3$	8.36 t	7.81 s	18.5
2b	2288	35	1090	628	$CDCl_3$	8.46 t	6.04 s 2.5–3.2 m	20.7
2c	2250	21	1088	626	CH_2Cl_2	8.38 t	2.3–3.0 m	37.5
2d	2285	31	1100	625	CH_2Cl_2	8.00 t	8.18 t^g	25.5
2e	2290	37	1090	624	CH_2Cl_2	8.02 t	6.26^h 2.2–3.3 m	29.2
2f	2253	24	1090	624	$CDCl_3$	7.84 t	2.2–3.2 m	44.4

[a] Very weak. [b] ν(complex) – ν(free). [c] Very strong. [d] Medium to strong. [e] J_P = ca. 8 Hz. [f] 10^{-3} M in CH_2Cl_2. [g] J_P = ca. 1.5 Hz. [h] Poorly resolved triplet.

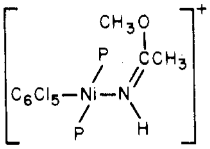
$(P)_2NCR]^+ClO_4^-$ (P = $PPhMe_2$, PPh_2Me), 2a–f. The chloride ligand in *trans*-$C_6Cl_5Ni(P)_2Cl$ (**1a**, P = $PPhMe_2$; **1b**, P = PPh_2Me) is labile and the complexes react readily with silver perchlorate even in a nonpolar solvent such as benzene resulting in the precipitation of silver chloride.[6] Addition of a slight excess of nitrile to the filtrate causes precipitation of a cationic pentachlorophenylnickel(II) complex, *trans*-$[C_6Cl_5Ni(P)_2NCR]^+ClO_4^-$, **2a–f** (see Table I), often as its benzene solvate, which can be converted to the unsolvated complex by recrystallization from methanol or ethanol or by heating below the melting point. The nitrile complexes thus prepared are air stable and readily soluble in dichloromethane to give conducting solution (Table II).[7] In common with almost all N-bonded nitrile complexes,[8] our products show a very weak band $\nu(C{\equiv}N)$ at higher frequencies than those of the free nitriles (Table II). The two bands near 1090 and 625 cm^{-1} are characteristic of the anionic (T_d) ClO_4^- group.[9]

The ^1H NMR spectra (Table II) are consistent with diamagnetic, trans planar structures in solution. A symmetrical 1:2:1 triplet resonance in the vicinity of τ 8 is assigned to the phosphine methyl protons, indicative of "virtually" coupled trans phosphines.[10] The spectrum of **2a** shows the nitrile methyl protons as a singlet downfield from free acetonitrile (τ 8.04), reflecting the decrease of electron density in this ligand on coordination to a cationic nickel moiety. The reverse shift in complex **2d** may be explained by the fact that the "neighbor anisotropy" effect[11] of the phenyl rings in the adjacent methyldiphenylphosphine ligands has overcome the electronic effect. An analogous result is obtained for the methylene protons of phenylacetonitrile (free, τ 6.28) complexes, **2b** and **2e**. Phosphine cis coupling was observed for the acetonitrile protons of complex **2d**.

Reactions of Nitrile Complexes with Alcohols. Complex **2a** reacts with methanol in the presence of triethylamine at a moderate temperature. The ir spectrum of the product, **3a**, shows no $\nu(C{\equiv}N)$ band but a strong band at 1661 cm^{-1} assignable to $\nu(N{=}C)$[5,12] and a weak band at 3260 cm^{-1} assignable to $\nu(N\text{—}H)$ in addition to characteristic bands due to perchlorate anion at 1110 (vs) cm^{-1}, the pentachlorophenyl group, and dimethyl(phenyl)phosphine. Those bands observed at 1238 and 1070 cm^{-1} can be assigned to the $\nu_a(COC)$ and $\nu_s(COC)$ vibrations,[5] respectively, although weaker bands due to the pentachlorophenyl group are expected to appear at these frequencies. These spectral observations, together with elemental analyses, are in accord with cationic pentachlorophenylnickel(II) complexes of the imidate, $NH{=}C(CH_3)OCH_3$. The ^1H NMR spectrum of this complex exhibits a triplet at τ 8.56 ($P\text{–}CH_3$), peaks at τ 8.72 and 8.32 ($C\text{–}CH_3$), and peaks at τ 6.96 and 6.73 (ratio 5:3) ($O\text{–}CH_3$). Thus, **3a** is considered to be a mixture of two isomers, **3aE** and **3aZ**.



3aE



3aZ

No distinct resonance was detected for the NH proton.

The perchlorate anion of **3a** can easily be replaced by hexafluorophosphate anion, and the ^1H NMR spectrum of this salt, **3a'**, was quite similar to that of **3a**. The acetonitrile complex **2a** also reacts with ethanol to give the corresponding imidate complex, **4a**, the ^1H NMR spectrum of which reveals two isomers in an ca. 8:5 ratio. Analytical and spectral data for such imidate complexes, prepared from **2a–e**, are given in Tables III and IV, respectively. In these reactions phenylacetonitrile complexes, **2b** and **2e**, which were recrystallized from ethanol without change, reacted with methanol even in the absence of triethylamine to give the corresponding imidate complexes, **3b** and **3e**; the higher acidity of methanol (pK_a 16) than of ethanol (pK_a 17) seems to be effective in a step of the reaction path.[13]

^1H NMR spectra of **3d** and **3e** indicate that only one isomer is present in each case, probably due to the steric influence of the phosphine phenyl groups. Another example of the difference in the phosphine ligands is manifest in the reactivities of complexes **2c** and **2f**; the former gives the imidate complex **3c** but **2f** does not react when treated in a similar manner.[13] In boiling methanol, complex **2f** decomposes; a detailed investigation of this and of other reactions is in progress.

The ^1H NMR spectra of these imidate complexes contain, in general, a 1:2:1 triplet of $P\text{–}CH_3$ protons, characteristic of trans square-planar coordination around nickel(II). The corresponding resonance pattern for **3c** in dichloromethane is complex with multiplet peaks centered at τ 8.60 and weak satellites at lower field. In deuterioacetone (Figure 1), the resonances are composed of a well-defined 1:1:2:2:1:1 sextet (or two 1:2:1 triplets) centered at τ 8.49 and a weak triplet at τ 8.35. Since the $O\text{–}CH_3$ proton resonances are composed

Table III. Analytical Data for Imidate-Nickel(II) Complexes, *trans*-$[C_6Cl_5Ni(P)_2NH{=}C(R)OR']^+X^-$

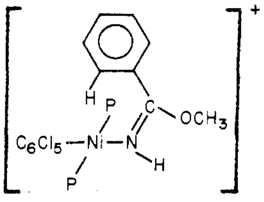
Complexes							% C		% H		% N	
No.	P	R	R'	X^-	Yield, %	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
3a	$PPhMe_2$	CH_3	CH_3	ClO_4^-	78	195–197	39.67	39.45	3.86	3.74	1.85	1.90
3a'		CH_3	CH_3	PF_6^-		203–204	37.42	37.54	3.64	3.33	1.75	1.82
3b		$CH_2C_6H_5$	CH_3	ClO_4^-	84	193–194	44.70	44.44	3.99	3.76	1.69	1.67
3c		C_6H_5	CH_3	ClO_4^-	47	175–177	44.00	43.75	3.82	3.55	1.71	1.94
3d	PPh_2Me	CH_3	CH_3	ClO_4^-	68	189–191	47.72	47.69	3.78	3.49	1.59	1.52
3e		$CH_2C_6H_5$	CH_3	ClO_4^-	84	193–194	51.45	51.35	3.90	3.65	1.46	1.47
4a	$PPhMe_2$	CH_3	C_2H_5	ClO_4^-	45	202–204	40.51	40.60	4.05	4.03	1.82	1.89

Table IV. Spectral Data for Imidate-Nickel (II) Complexes

	Ir spectra, cm^{-1}		^1H NMR spectra[a]			
Complex	$\nu(N{-}H)$	$\nu(N{=}C)$	Solvent	$\tau(P{-}CH_3)$,[b] ppm	$\tau(O{-}CH_3)$ or $\tau(O{-}CH_2)$,[c] ppm	Others,[d] ppm
3a	3260 w	1661 s	CH_2Cl_2[e]		6.96 (5) s, 6.37 (3) s	8.72 s, 8.32 s, 2.67
3a'	3350 m	1649 s	CH_2Cl_2	8.57 t	6.91 (3) s, 6.49 (2) s	8.65 s, 8.37 s, 2.66
3b	3316 w	1623 s	CH_2Cl_2[f]	8.62 t	6.39 (5) s, 6.31 (1) s	6.81 s, 6.54 s, 3.1–2.5
3c	3240 m	1623 s	$(CD_3)_2CO$[e]		6.12 (7) s, 5.81 (2) s	2.9–2.1, 0.93 d[g]
3d	3270 w	1649 s	CH_2Cl_2	8.10 t	6.84 s	8.30 s, 2.8–2.1
3e	3270 w	1638 s	CH_2Cl_2	8.08 t	6.31 s	6.63 s, 3.8–2.4
4a	3250 w	1655 s	CH_2Cl_2	8.54 t	6.84 (8) q, 6.12 (5) q[h]	9.0–8.1, 2.67

[a] Data for solutions at 23 °C. [b] J_P = ca. 7–8 Hz. [c] Intensity ratio is shown in parentheses. [d] $\tau(C{-}CH_3)$, $\tau(C{-}CH_2)$, and $\tau(C_6H_5)$. [e] See text for $\tau(P{-}CH_3)$. [f] Saturated solution. [g] J_H = ca. 7 Hz. [h] J_H = ca. 7 Hz.

of two peaks at τ 6.12 and 5.81 with an intensity ratio of 7:2, the presence of two isomers is expected as discussed above for **3a**. Observation of such a sextet is indicative of an imidate ligand fixed perpendicularly to the nickel coordination plane resulting in two distinctive P–CH_3 groups.[14] Of interest is the observation of a doublet at low field, τ 0.93, with intensity corresponding to ca. one proton. This observation, together with the above results, is fully in agreement with the structural assignment for the main isomer I, in which one ortho ring



I

proton on the phenyl group in the imidate ligand is situated directly over and close to the coordination plane, where the paramagnetic anisotropy of the nickel(II) ion is pronounced.[15] On the other hand, the spectra of **3a** in dichloromethane show two triplets (τ 8.13 and 8.96) at −60 °C, three triplets (τ 8.18, 8.56, and 8.86) at −5 °C, and one triplet (τ 8.54) at 45 °C, indicating that the rotation around Ni–N bond is frozen in both isomers at −60 °C, frozen in one isomer but free in the other at −5 °C, and free in both isomers at 45 °C on the ^1H NMR time scale. The large differences in rotational barriers which are expected to exist for the two isomers may be explained in terms of steric influence rather than double-bond character in the Ni–N bond. Due to the presence of C–CH_3 proton resonances in the region, a more detailed investigation has not been performed.

Substitutions of the Acetonitrile Ligand. The acetonitrile ligand in complex **2a** is easily replaced in methanol by a halide anion (Br, I, NCS) or by the acetate anion to give the corresponding neutral complex *trans*-$C_6Cl_5Ni(PPhMe_2)_2X$. Trimethyl phosphite also reacts to give the cationic complex *trans*-$[C_6Cl_5Ni(PPhMe_2)_2P(OMe)_3]^+ClO_4^-$. Easy replacement of acetonitrile coordinated to a transition metal has recently been reported.[5,16,17] The ease of such replacements can be attributed to the weak coordination bond and less steric hindrance. A positive charge and the coordinative unsaturation of complex **2a** might also be expected to enhance donor interaction.

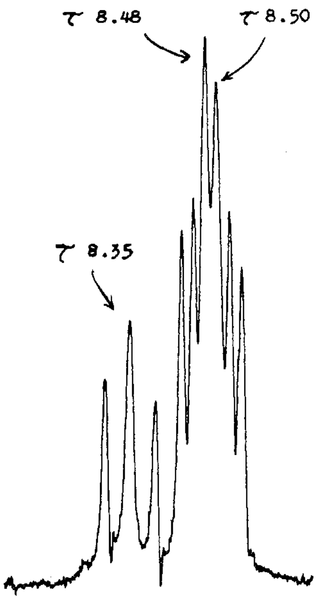


Figure 1. ^1H NMR spectra of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2$-$NH{=}C(Ph)OMe]^+ClO_4^-$, recorded on a deuterioacetone solution.

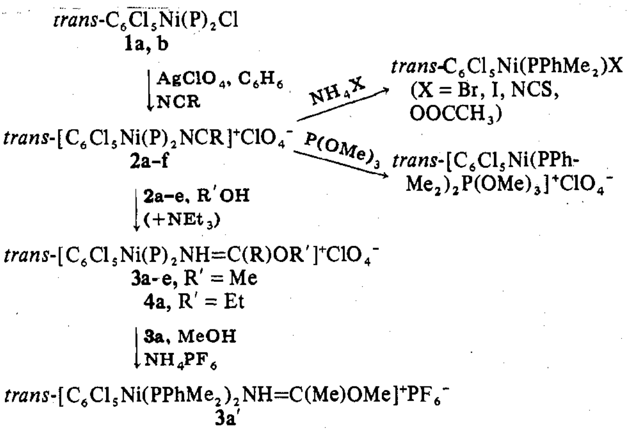
The reactions studied in the present work are summarized in Scheme I.

Experimental Section

Both *trans*-$C_6Cl_5Ni(PPhMe_2)_2Cl$, **1a**, and *trans*-C_6Cl_5Ni-$(PPh_2Me)_2Cl$, **1b**, were prepared as described previously.[6] Commercial grade silver perchlorate and nitriles were used. Ir spectra were recorded on a Hitachi 225 spectrophotometer over the range 4000–700 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the range 700–200 cm^{-1} using Nujol mulls. ^1H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to TMS as an internal standard.

Preparation of *trans*-$[C_6Cl_5Ni(P)_2NCR]^+ClO_4^-$, 2a–f. Nitrile complexes **2a–f** were prepared essentially by the same procedures, so only two representative examples are described. Percentage yields and analytical data are shown in Table I; spectral and conductivity data are shown in Table II.

Scheme I



P = $PPhMe_2$ (**1a**, **2a–c**, **3a–c**, **4a**), PPh_2Me (**1b**, **2d–f**, **3d**, **3e**); R = Me (**2a**, **2d**, **3a**, **3d**, **4a**), CH_2Ph (**2b**, **2e**, **3b**, **3e**), Ph (**2c**, **2f**, **3c**)

A solution of **1a** (3.10 g, 5.0 mmol) in benzene (50 ml) was added dropwise to a solution of a slight excess of silver perchlorate (1.12 g) in benzene (150 ml). The silver chloride precipitate was removed by filtration to give an orange-brown solution, to which an excess of acetonitrile (2.5 ml) was added with stirring, followed by ca. $^1/_3$ volume of *n*-hexane. The resulting orange-yellow precipitate was separated by filtration and washed with benzene and air-dried to give orange-yellow crystals of **2a**.

A solution of **1b** (0.744 g, 1.0 mmol) in benzene (10 ml) was added dropwise to a solution of silver perchlorate (0.208 g, 1.0 mmol) in benzene (20 ml). The silver chloride precipitate was removed by filtration to give an orange-brown solution, to which an excess of phenylacetonitrile was added with stirring, followed by ca. $^1/_3$ volume of *n*-hexane. The resulting orange-yellow precipitate was separated by filtration and recrystallized from ethanol to give orange-yellow crystals of **2e**.

Complex **2b** prepared by the same procedure as above was recrystallized from ethanol. Complex **2c** prepared by the same procedure as above was heated at 130 °C for several hours to give the unsolvated complex. Complexes **2d** and **2f** were recrystallized from methanol.

Reactions of 2a–f with Alcohol. Complex **2a** (0.725 g, 1.0 mmol) was dissolved in methanol (20 ml) with minimum heating. To the solution was added 1 drop of triethylamine and the mixture was cooled to 0 °C to give an orange-yellow precipitate (0.700 g, mp 189–191 °C), which was recrystallized from methanol (10 ml) to give crystals of **3a** (Tables III and IV).

Treatment of **2a** with ethanol in a similar manner as above and recrystallization of the product from acetone–ethanol (10:20) gave orange-yellow crystals of **4a**.

When **2b** was treated in methanol in a similar manner as above, the solution deposited orange crystals of **3b** at room temperature. Complex **2b** was also found to react with methanol even in the absence of triethylamine to give a mixture of complex **2b** and **3b**, the latter being the major product.

Complex **2c** was treated in methanol in a similar manner as **2a**. The product (mp ca. 160 °C) was extracted with boiling methanol leaving a small amount of unidentified orange crystals (the identification is in progress). The filtrate was concentrated and upon refrigeration gave orange-yellow crystals of **3c**.

Complex **2d** was treated in methanol in a similar manner as **2a**, and the product **3d** was subjected to elemental analysis without recrystallization.

Complex **2e** was dissolved in methanol and the solution was kept at room temperature for 24 h to give the orange-yellow crystals of **3e**.

Complex **2f** was recovered when treated with methanol even in the presence of a large excess of triethylamine but seemed to decompose when the solution was refluxed for a long time. Further investigations are in progress.

Percentage yields, melting points, and analytical data are shown in Table III; spectral data are shown in Table IV.

Anion Exchange of Complex 3a. Repeated crystallizations of complex **3a** from methanol containing an excess of ammonium hexafluorophosphate gave crystals of the salt **3a′**, of which analytical and spectral data are also shown in Tables III and IV.

Substitutions of Acetonitrile Ligand in 2a. To a hot solution of complex **2a** (0.290 g, 0.40 mmol) in methanol (10 ml) was added a solution of ammonium halide (a slight excess) in methanol (5 ml). The mixture was cooled to room temperature to give the crystals of *trans*-$C_6Cl_5Ni(PPhMe_2)_2X$. Both **bromide** [brown crystals, yield 90%, mp 181–182 °C (lit.[14] 179–181 °C)] and **iodide** [dark brown crystals, yield 88%, mp 168–170 °C (lit.[14] 166–169 °C)] were identified by their melting points and ^1H NMR spectra. The **thiocyanate** appeared as yellow-brown crystals, yield 87%, mp 173–174 °C. Anal. Calcd for $C_{23}H_{22}NCl_5P_2SNi$: C, 43.00; H, 3.45; N, 2.18; mol wt 642.4. Found: C, 42.98; H, 3.51; N, 2.17; mol wt 644 (VPO method in $CHCl_3$). The ir spectrum showed the ν(NCS) at 2089 (vs) cm^{-1}.

A mixture of **2a** (0.40 mmol) and ammonium **acetate** (ca. 0.2 g, a large excess) in methanol (10 ml) was stirred at room temperature to give an orange-yellow solution. Water (ca. 10 ml) was added, and the precipitate was recrystallized from *n*-hexane to give yellow-brown crystals of *trans*-$C_6Cl_5Ni(PPhMe_2)_2OOCCH_3$, yield 0.188 g, 73%, mp 127–128 °C. Spectra: ir, $\nu_a(CO_2)$ 1612 cm^{-1}; ^1H NMR (CH_2Cl_2), $\tau(P–CH_3)$ 8.56 t, $\tau(C–CH_3)$ 8.50 s. Anal. Calcd for $C_{24}H_{25}O_2Cl_5P_2Ni$: C, 44.80; H, 3.92. Found: C, 44.99; H, 4.07.

To a hot solution of **2a** (0.40 mmol) in methanol (10 ml) was added **trimethyl phosphite** (0.07 ml), and the solution was cooled to 0 °C to give crystals of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2P(OMe)_3]^+ClO_4^-$, yield 58%, mp 179–180 °C. Spectra: ir, ν(POC) 1000 cm^{-1}, $\nu(ClO_4^-)$ 1072 cm^{-1}; ^1H NMR (CH_2Cl_2) $\tau(P–CH_3)$ 8.38 t, $\tau(O–CH_3)$ 6.47 d. Anal. Calcd for $C_{25}H_{31}O_7Cl_6P_3Ni$: C, 37.17; H, 3.87. Found: C, 36.90; H, 3.86.

Registry No. **1a**, 15526-04-2; **1b**, 26025-08-1; **2a**, 58280-94-7; **2b**, 58280-96-9; **2c**, 58280-98-1; **2d**, 58281-00-8; **2e**, 58281-02-0; **2f**, 58281-04-2; **3aE**, 58281-06-4; **3aZ**, 58341-89-2; **3a′E**, 58281-07-5; **3a′Z**, 58341-90-5; **3bE**, 58281-09-7; **3bZ**, 58341-92-7; **3cE**, 58281-11-1; **3cZ**, 58341-94-9; **3d**, 58281-13-3; **3e**, 58281-15-5; **4aE**, 58281-17-7; **4aZ**, 58341-96-1; *trans*-$C_6Cl_5Ni(PPhMe_2)_2Br$, 15526-05-3; *trans*-$C_6Cl_5Ni(PPhMe_2)_2I$, 15526-06-4; *trans*-$C_6Cl_5Ni(PPhMe_2)_2(NCS)$, 58281-18-8; *trans*-$C_6Cl_5Ni(PPhMe_2)_2(OOCCH_3)$, 58281-19-9; *trans*-$[C_6Cl_5Ni(PPhMe_2)_2P(OMe)_3]^+ClO_4^-$, 58281-21-3; methanol, 67-56-1; ethanol, 64-17-5; trimethyl phosphite, 121-45-9.

References and Notes

(1) (a) K. Sakai, T. Ito, and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **40**, 1660 (1967); (b) S. Komiya, S. Suzuki, and K. Watanabe, *ibid.*, **44**, 1440 (1971); (c) R. Breslow, R. Fairweather, and J. Keana, *J. Am. Chem. Soc.*, **89**, 2135 (1967); (d) R. Breslow and M. Schmir, *ibid.*, **93**, 4960 (1971); (e) D. Pinnell, G. B. Wright, and R. B. Jordan, *ibid.*, **94**, 6104 (1972); (f) D. A. Buckingham, F. R. Kneene, and A. M. Sargeson, *J. Am. Chem. Soc.*, **95**, 5649 (1973); (g) K. B. Nolan and R. W. Hay, *J. Chem. Soc., Dalton Trans.*, 914 (1974); (h) C. R. Clark and R. W. Hay, *ibid.*, 2149 (1974).

(2) (a) P. F. D. Barnard, *J. Chem. Soc. A*, 2140 (1969); (b) S. Suzuki, M. Nakahara, and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 1441 (1971).

(3) (a) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971); (b) T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *ibid.*, **11**, 1786 (1972); (c) H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, **47**, C17 (1973); (d) L. E. Manzer, *J. Chem. Soc., Dalton Trans.*, 1535 (1974).

(4) R. Ros, J. Renaud, and R. Roulet, *J. Organomet. Chem.*, **87**, 379 (1975).

(5) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 489 (1968).

(6) M. Wada, *Inorg. Chem.*, **14**, 1415 (1975); other chloro(organo)nickel(II) complexes like *trans*-*o*-$CH_3C_6H_4Ni(PPhMe_2)_2Cl$ decompose during a similar reaction with silver perchlorate.

(7) In dichloromethane molar conductance values for 10^{-3}, 10^{-4}, and 10^{-5} M solutions of $(C_2H_5)_4NClO_4$ were 22.2, 52.7, and 92.0 ohm^{-1} cm^2 mol^{-1} by our measurement, in good agreement with the reported value 53 at 10^{-4} M [P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Am. Chem. Soc.*, **93**, 5424 (1971)]. On the other hand a value of 78.0 for $(C_6H_5)_4AsCl$ has been taken as the reference value for a 1:1 electrolyte at $\sim 10^{-3}$ M, and complexes of type [CpNi(diphos)]X have been reported to show a value in the range 57–39 [L. A. Kaemphe and K. W. Barnett, *Inorg. Chem.*, **12**, 2578 (1973)]. From these facts the values observed for our complexes in Table I are in the region between the two reference values for a 1:1 electrolyte, and the inconstancy may be due to some ion pairing. The use of solvents in which ion pairing is less important, e.g., water, methanol, or acetonitrile, is precluded by the reactivity or by the poor solubility of some of the complexes.

(8) R. A. Walton, *Q. Rev., Chem. Soc.*, **19**, 126 (1965).

(9) (a) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); (b) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

(10) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(11) J. A. Pople, W. G. Schneider, and H. J. Benstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, p 176.

(12) H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3724 (1965).
(13) The higher reactivity of phenylacetonitrile complexes than that of acetonitrile complexes is tentatively explained in terms of the inductive effect of phenyl group, and the lower reactivity of benzonitrile complex **2f** than that of acetonitrile complex **2d** may alternatively be attributed to the mesomeric effect, which causes a delocalization of the induced positive charge on coordination to a cationic nickel moiety in the phenyl group.
(14) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1793 (1966).
(15) (a) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Am. Chem. Soc.*, **92**, 1511 (1970); (b) D. R. Fahey, *J. Organomet. Chem.*, **57**, 385 (1973).
(16) C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1365, 1370 (1973).
(17) R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 808 (1974).

Contribution from the Institute of Inorganic and Analytical Chemistry,
Joh. Gutenberg-Universität, D-6500 Mainz, Germany

New Aspects of the High Spin–Low Spin Transition in Tris(2-methyl-1,10-phenanthroline)iron(II) Perchlorate

J. FLEISCH, P. GÜTLICH,* K. M. HASSELBACH, and W. MÜLLER*

Received July 14, 1975 AIC50487E

The high spin–low spin transition in the polycrystalline complex compound $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ ($2\text{-}CH_3phen$ = 2-methyl-1,10-phenanthroline) has been reinvestigated by Mössbauer measurements at 21 temperatures between 4.2 and 295 K, magnetic susceptibility measurements down to 2.6 K, and ir and far-ir spectroscopy. The far-ir spectra at 298 and 108 K exhibit distinct absorption lines characteristic of high-spin and low-spin Fe–N vibrations. Two high-spin iron(II) quadrupole doublets are observed in the Mössbauer spectra, which are interpreted as arising from two different lattice sites for high-spin iron(II); apparently both of them convert into one and the same low-spin state appearing as a characteristic quadrupole doublet. From a theoretical analysis of the temperature dependence of the quadrupole splitting, with trigonal field distortion, spin–orbit coupling, and effects of covalency taken into account, it can be shown that the two high-spin iron(II) doublets can be attributed to iron(II) in ^5E and $^5A_1$ ground states respectively, under D_3 symmetry. Anomalous magnetic behavior and a discontinuity in several Mössbauer parameters in the temperature range 70–100 K have been detected; these are believed to originate from a phase transition.

Introduction

The high spin–low spin transition in $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ ($2\text{-}CH_3phen$ = 2-methyl-1,10-phenanthroline) has been well established by magnetic[1] and Mössbauer[2] measurements. In connection with Mössbauer emission spectroscopy on ^{57}Co-labeled diimine complexes of cobalt(II) performed in our laboratory a more profound knowledge of the magnetic behavior of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ was desirable. As already partly reported in a preliminary publication,[3] Mössbauer effect measurements at 21 temperatures between 4.2 and 295 K confirm the existence of the spin transition, but in contrast to the earlier publication[2] two ferrous high-spin doublets are apparent from the spectra.

Earlier magnetic susceptibility studies by Goodwin et al.[1] had been carried out in the temperature range 300–90 K. To learn more about the low-temperature magnetism we have extended the magnetic measurements down to 2.6 K. Moreover, from far-ir spectra taken at room temperature and 108 K we hoped to gain specific signals on vibrational properties above and below the magnetic crossover.

Experimental Section

The complex $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ was prepared according to the method of Pfeiffer and Christeleit[4] by adding an aqueous solution containing excess sodium perchlorate to a solution of stoichiometric amounts of ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, and the ligand[5] dissolved in a water–methanol mixture (1:1). The product was recrystallized from water–methanol and dried under vacuum with phosphorus pentoxide.

The magnetic susceptibility data were recorded with a Foner-type magnetometer calibrated with nickel metal. Temperatures between 2 and 300 K at the sample could be obtained by means of a continuous-flow cryostat. The temperature was measured with a gallium arsenide diode (accuracy ≥0.5%). The maximum error of the susceptibility data is estimated to be 1%. Effective magnetic moments, μ_{eff}, were calculated using the formula

$$\mu_{eff} = 2.8273\sqrt{\chi'_m T} \qquad (1)$$

where χ'_m is the molar susceptibility corrected for diamagnetism (505 $\times 10^{-6}$ emu mol^{-1} calculated according to Figgis and Lewis[6]).

Table I. Characteristic Bands in the Far-Ir Spectra of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ at 108 and 298 K and of the Free Ligand at 298 K (in Parentheses)

Wavenumber $\tilde{\nu}$, cm^{-1}		
108 K	298 K	Assignment
419 s	419 s (405 w)	Ligand
348 m	348 w, sh (348 s)	
331 w	330 w	
318 w, sh	310 (305)	Ligand
283 w		ν(Fe–N) (low spin)
270 w, sh		
247 s	247 s (245 m, sh)	Ligand
231 s		δ(N–Fe–N) (low spin)
216 s	213 s	ν(Fe–N) (high spin)
190 m, sh	185 m, sh (190 s, br)	Ligand
73 m	68 m (72 m)	

The far-infrared spectra (50–500 cm^{-1}) were measured at 298 and 108 K, using a Polytec FIR 30 spectrometer (polyethylene pellets).

The Mössbauer spectra were taken with a constant-acceleration electromagnetic drive operating in the multiscaling mode. The source ^{57}Co–Cu was kept at room temperature. The absorber temperature was varied between 4.2 and 300 K, with a constancy of ±0.1 K. The absorbers contained about 0.15 mg of $^{57}Fe/cm^2$.

Results

The far-ir spectra contain a number of bands which are essentially identical with those of the free ligand (in Table I the free ligand vibrations at room temperature are given in parentheses) and are practically not shifted by changing the temperature. The Fe–N vibrations with temperature-dependent intensities occur in the region of ca. 330–213 cm^{-1}. Their assignment is possible by comparison with far-ir spectra of similar iron–diimine complexes from the literature.[7,8] The bands at 213 cm^{-1} (298 K) and 216 cm^{-1} (108 K) can be assigned to the high-spin Fe–N stretching vibration. The absorption lines with the center of gravity at about 300 cm^{-1} in the low-temperature spectrum should contain low-spin Fe–N stretching vibrations, but the assignment is complicated by a ligand absorption occurring in the same region. The band at