Consideration for the asymmetry parameter (κ) was another important feature of this analysis. This parameter and its influence on the others have been examined throughout the refinements concurrently with other changes in the procedure. The first and second peaks on the experimental radial distributions display asymmetries in opposite directions. The Ca–X peaks are broader at the larger r values whereas the X···X peaks are broader at the smaller r values. Anharmonicity in the vibrations as well as the relevant contributions from the dimers are consistent sources for such asymmetries. Inclusion of κ parameters proved to be important for the M–X distance whereas this made no difference for the X···X distance. The influence of this parameter is felt increasingly at higher s values. The contributions of the X···X distances, especially with increasing atomic number of X, however, quickly diminish. On the other hand, examination of the κ parameter for the bond of $CaCl_2$ at least partially resolved the puzzle of the large discrepancy between our r(Ca–Cl) value and the result of the reinvestigation by Spiridonov et al.[12] Ignoring this parameter, we could decrease our Ca–Cl bond length by 0.015 Å, thus bringing it closer to the very low value cited.[12] The asymmetry parameter was ignored in the latter work.

The parameter κ is usually estimated as $\kappa = al^4/6$, where a is related to the Morse constant and is usually assumed to be 2 $Å^{-1}$. Such an assumption for Ca–Cl would give $\kappa = 5.8 \times 10^{-5}$ $Å^3$. The value obtained in our refinement is twice as large, and the corresponding change in the bond length is 1 standard deviation. The uncertainty in the asymmetry parameter as well as the uncertainty in the dimer content have been included as additional error source components in the estimated total errors.

In the matter of the discrepancy of our r(Ca–I) value and that of Kasparov et al., our various test calculations offered no obvious origin. However, the difference is within the combined experimental errors.

Registry No. $CaCl_2$, 10043-52-4; $CaBr_2$, 7789-41-5; CaI_2, 10102-68-8.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera ranges (50 and 19 cm) for all three compounds (6 pages). Ordering information is given on any current masthead page.

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Conformational Behavior of Co–tn Chelate Rings in Complex Compounds (tn = 1,3-Propanediamine) and Their Infrared Spectra

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Joachim Degen,[‡] and Hans Kupka[§]

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In a previous study,[1] the ground-state geometry of *trans*-$[Co(CN)_2(tn)_2]^+$ in two different crystals was studied by X-ray structural analysis. It was found that in the chloride trihydrate crystal, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$, both six-membered tn–metal chelate rings of the complex *trans*-$[Co(CN)_2(tn)_2]^+$ assume the chair form, while in the chloride monohydrate crystal one is present in the chair and the other in the skew-boat form. Moreover, by analysis of the vibronic fine structure of the electronic absorption spectrum as well as by MO calculations, the distortion of *trans*-$[Co(CN)_2(tn)_2]^+$ in one of its d-electronic excited states was deduced relative to the ground state. This distortion results in a flattening of the chelate rings in the equatorial direction, as well as a contraction along the vertical axis containing the cyanide ligands. In this paper, information obtained from the infrared spectra of the above mentioned metal complexes as well as related complexes was used for a conformational analysis of the chelate rings. We performed a normal-coordinate analysis confined to a Co–tn ring and a conformational analysis of the chelate rings to assign the solid-state and solution spectra.

Experimental Section

The preparation and properties of crystals of *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$, and their N- and O-deuteriated compounds were reported previously.[1] The complex compounds *trans*-$[CoCl_2(tn)_2]Cl{\cdot}HCl{\cdot}2H_2O$,[2] *trans*-$[CoCl_2(tn)_2]Cl$,[3] *trans*-$[Co(NO_3)_2(tn)_2](NO_3)$,[4] $[Co(tn)_3]Cl_3$,[3] $[Cr(tn)_3]Cl_3{\cdot}4H_2O$,[5] and $[Cr(tn)_3][Ni(CN)_5]{\cdot}2H_2O$[6] were prepared by standard methods.

Infrared absorption spectra of the solid samples were recorded in the Nujol phase. The measurements at −15 °C were successfully performed by using a cooled sample holder in a small compartment equipped with KBr windows. The solution (D_2O) IR spectroscopy was performed with a 0.05-mm cell consisting of two KBr plates coated by thin polyethylene film with the entire sample system placed into a vigorous air stream controlled at various temperatures from 15 to 55 °C. The temperature was monitored by a thermocouple inserted between the KBr plates, which hold the Nujol mull. Small amounts of DCl were added to the D_2O solution in the case of the H compound in order to prevent deuteriation of the N hydrogens.

The ^{13}C NMR signals of solid samples were measured by the cross-polarization magic-angle spinning (C/P MAS) technique on a JEOL JNM-GX270 spectrometer equipped with a C/P MAS accessory (NM-GSH270). Samples were spun at 3–4 kHz. The pulse repetition time and the cross-polarization contact time were 5 s and 2 ms, respectively. Each spectrum required from 10000 to 30000 scans. Chemical shifts were measured with respect to Me_4Si via adamantane as a secondary substitution reference (29.5 ppm).

Normal-coordinate analyses were carried out at the Computer Center of Tokyo University, using the library programs BGLZ and LSMB written by Shimanouchi et al.[7]

Results and Discussion

The IR spectra of various Co(III) complexes containing equatorially oriented Co–tn chelate rings are shown in Figure 1. The spectrum in the region 800–1100 cm^{-1} of the solid *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$ is essentially the same as those of *trans*-$[CoCl_2(tn)_2]Cl{\cdot}HCl{\cdot}2H_2O$ and *trans*-$[Co(NO_3)_2(tn)_2]NO_3$, except for a peak that can be explained as arising from NO_3^-. These compounds were confirmed by X-ray diffraction[1,8,9] to have two chair rings arranged in a centrosymmetric C_{2h} molecular symmetry. However, the complex compound *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$ has only one six-membered chelate ring in the chair and the other in the skew-boat form.[1] This difference in geometry is manifest by the appearance of an additional peak in this region. That is, three distinct peaks at 896, 922, and 959 cm^{-1} were observed for the monohydrated compound, while the trihydrate gives only two peaks at 890 and 933 cm^{-1}. Similarly, the complex cation *trans*-$[Co(CN)_2(tn)_2]^+$ in D_2O solution has only two IR absorption bands in this region.

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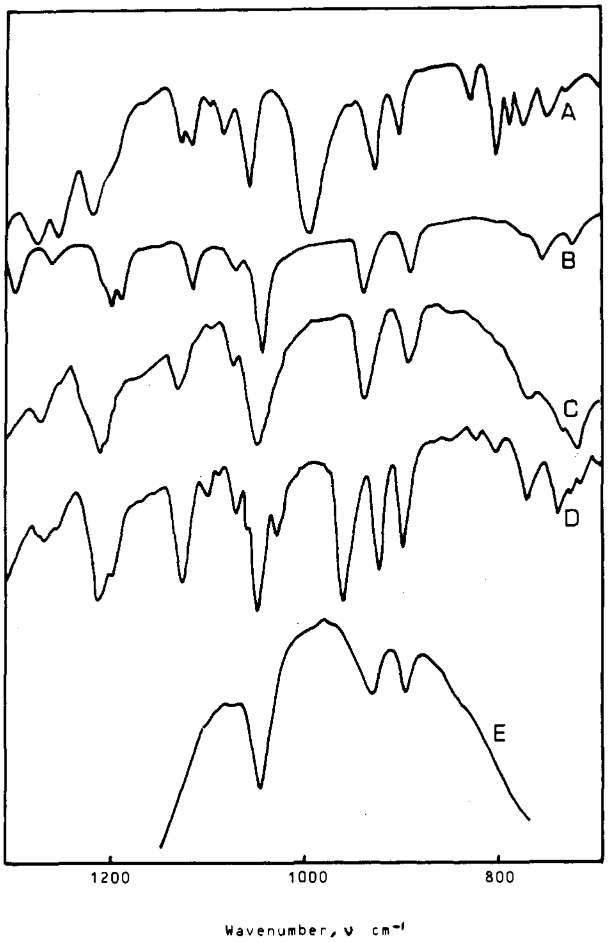

Figure 1. Infrared absorption spectra of *trans*-$[CoX_2(tn)_2]^+$ type complexes: A, *trans*-$[Co(NO_3)_2(tn)_2]NO_3$ in Nujol phase; B, *trans*-$[CoCl_2(tn)_2]Cl{\cdot}HCl{\cdot}2H_2O$ in Nujol phase (the absorption spectrum of *trans*-$[CoCl_2(tn)_2]Cl$ in Nujol phase appeared very similar to this spectrum); C, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$ in Nujol phase (at −15 °C); D, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$ in Nujol phase; E, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$ in D_2O (DCl).

While the carbon atoms included in the two-chair structure can be classified stereochemically into two categories, i.e., N–*C*–C and C–*C*–C, all of the carbon atoms in the one-chair–one-skew-boat structure are magnetically nonequivalent. This is recognizable in the solid-state ^{13}C NMR spectra shown in Figure 2. The clear ^{13}C signals of *trans*-$[Co(NO_3)_2(tn)_2]NO_3$ at 26 and 39 ppm are readily assigned to C–*C*–C and N–*C*–C resonances,[10] respectively. On the other hand, the powdered sample of *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$ showed an appreciable splitting of the corresponding signals, which can be rationalized as arising from deviation of the tn–Co–tn arrangement from C_{2h} symmetry. Thus, the spectral characteristics of the solid-state ^{13}C NMR spectra are extraordinarily informative about the spatial configurations of the individual chelate molecules. In the case of *trans*-$[CoCl_2(tn)_2]Cl$, the C/P MAS ^{13}C NMR signals indicate that both rings adopt the chair conformation (Figure 2). This is in accord with our findings based on vibrational spectroscopy (see below).

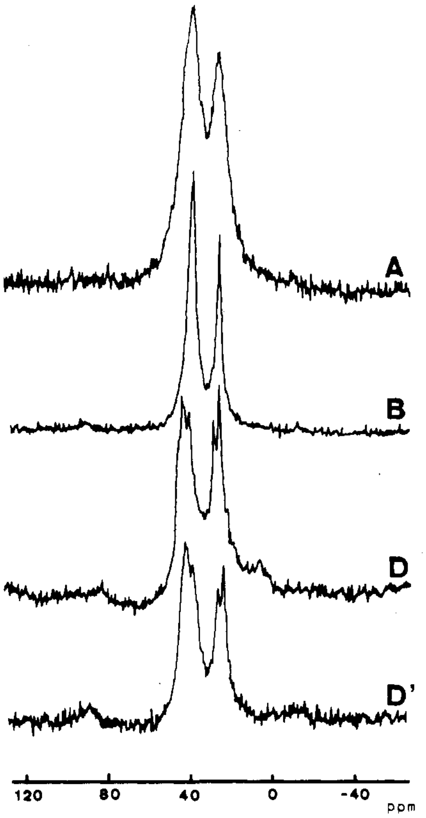

Figure 2. C/P MAS ^{13}C NMR signals: A, *trans*-$[Co(NO_3)_2(tn)_2]NO_3$; B, *trans*-$[CoCl_2(tn)_2]Cl$; D, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$; D′, *trans*-$[Co(CN)_2(tn\text{-}N,N,N',N'\text{-}d_4)_2]Cl{\cdot}D_2O$.

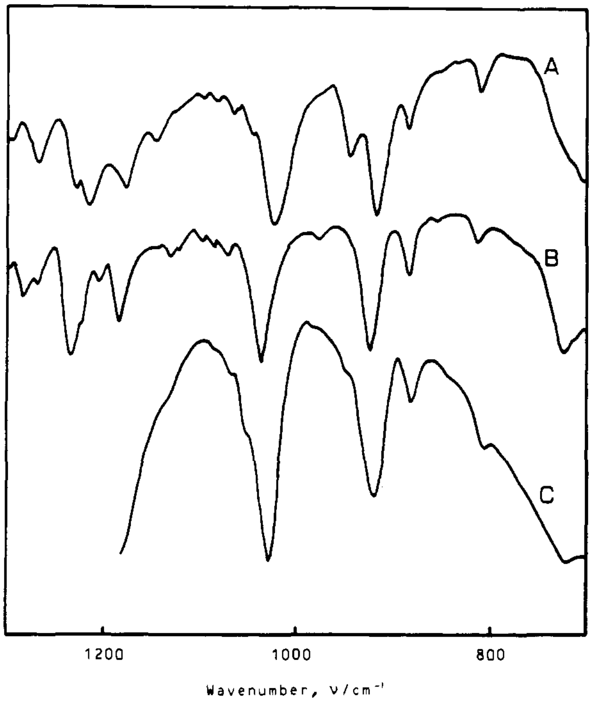

Figure 3. Infrared absorption spectra of $[Cr(tn)_3]^{3+}$ complexes: A, $[Cr(tn)_3][Ni(CN)_5]{\cdot}2H_2O$ in Nujol phase; B, $[Cr(tn)_3]Cl_3$ in Nujol phase; C, $[Cr(tn)_3]Cl_3$ in D_2O (DCl).

A closely analogous situation seems to exist in the series of complexes containing three M–tn rings (see Figure 3). Here the IR spectrum of $[Cr(tn)_3][Ni(CN)_5]{\cdot}2H_2O$, where one of the chelate rings has a skew-boat conformation while the other two have chair forms,[6] exhibits three distinct peaks at 883, 918, and 948 cm^{-1}. The powder sample of $[Cr(tn)_3]Cl_3{\cdot}4H_2O$ shows clearly two peaks in this region, at 884 and 924 cm^{-1}. There is no change in going from solid-state to D_2O spectra, except for a weak shoulder at ca. 950 cm^{-1} in the solution spectrum (curve C in Figure 3). This shoulder coincides in frequency with the peak at 949 cm^{-1} of the solid sample of $[Cr(tn)_3][Ni(CN)_5]{\cdot}2H_2O$ and could result from the fraction of $[Cr(tn)_3]Cl_3$ in D_2O solution that contains one chelate ring in a skew-boat conformation (see below). For $[Co(tn)_3]Cl_3$ the observed data are similar. The infrared spectrum of solid $[Co(tn)_3]Cl_3$ shows two peaks at 888 and 932 cm^{-1}. In the D_2O solution of $[Co(tn)_3]^+$ the peaks appear at 890 and 932 cm^{-1}, respectively, and the shoulder appears at ca. 950

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Table I. Vibrational Frequencies of the M–tn Ring in the Region 800–1100 cm^{-1} [a]

Chair Form (C_s symm)

normal vib (symm)	freq (ν), cm^{-1} calcd −6°	0°	+6°	obsd	PED[b]
$\nu_{28}(A')$	1042	1039	1035	1046,[c] 1048[d]	43 (side CCH, NCH), 18 (CC), 16 (top CCH)
$\nu_{29}(A'')$	1004	1004	1003		57 (NC), 20 (CC)
$\nu_{30}(A')$	898	900	904	933,[c] 922[d] 890,[c] 896[d]	27 (top CCH), 19 (NCoN), 19 (NCC), 12 (side CCH, NCH)
$\nu_{31}(A'')$	882	881	879		90 (side CCH, NCH)
$\nu_{32}(A')$	857	855	853		53 (CC), 25 (side CCH, NCH)

Skew-Boat Form (C_2 symm)

normal vib (symm)	freq (ν), cm^{-1} calcd 0°	+6°	+12°	obsd	PED[b]
$\nu_{28}(B)$	1038	1038	1038	1026[d]	28 (NC), 21 (CC), 20 (top CCH), 11 (NCC)
$\nu_{29}(A)$	954	953	953	959[d]	41 (side CCH, NCH), 19 (CC), 11 (CCC), 11 (NC), 11 (NCoN)
$\nu_{30}(B)$	949	949	948		51 (side CCH, NCH), 22 (NC), 20 (top CCH)
$\nu_{31}(A)$	854	856	860	848[d] 821[d] 801[d]	43 (CC), 15 (CoNH, CNH), 12 (side CCH, NCH), 11 (NCC)
$\nu_{32}(A)$	821	824	830		27 (CoNH, CNH), 19 (side CCH, NCH), 15 (NCoN)

[a] Force constants [K, H, F (mdyne/Å)]: K(Co–N) = 1.593, K(N–C) = 3.20, K(C–C) = 2.542, K(N–H) = 5.61, K(C–H) = 3.972, H(N–Co–N) = 1.531, F(N–Co–N) = 0.300, H(Co–N–C) = 0.10, F(Co–N–C) = 0.10, H(N–C–C) = 0.33, F(N–C–C) = 0.30, H(C–C–C) = 0.50, F(C–C–C) = 0.40, H(Co–N–H) = 0.19, F(Co–N–H) = 0.10, H(C–N–H) = 0.24, F(C–N–H) = 0.40, H(H–N–H) = 0.546, F(H–N–H) = 0.10, H(N–C–H) = 0.26, F(N–C–H) = 0.54, H(C–C–H) = 0.219, F(C–C–H) = 0.475, H(H–C–H) = 0.537, F(H–C–H) = 0.215. [b] Total contribution of equivalent internal coordinates. [c] *trans*-$[Co(CN)_2(tn)_2]Cl\cdot 3H_2O$. [d] *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$.

cm^{-1}. The two peaks at 900 and 920 cm^{-1} reported previously in the IR spectrum of $[Pt(tn)_2][PtCl_4]$[11] are probably a manifestation of the fact that both Pt–tn rings adopt the chair conformation.

Evidence for the experimental findings can be given by inspection of the normal modes of vibrations confined mainly to the M–tn ring. This makes it necessary to perform a normal-coordinate analysis. In the normal-coordinate analysis we have restricted ourselves to the six-membered-ring moiety of either the chair or skew-boat conformation, neglecting the interaction between the rings. This interaction is quite small in the region from 700 to 1000 cm^{-1} and can be neglected. The coordinates of atoms in the chair and the skew-boat conformers were taken from the X-ray structural analysis of *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$,[1] according to which the rings have point symmetries C_s and C_2, respectively. The force constants taken were those in a recent paper[1] and in ref 12. The calculated and observed frequencies and the potential energy distribution (PED) are listed in Table I. It was found that the normal modes in the range 700–1000 cm^{-1} are mixtures of primarily $-CH_2$ rocking motions of side and/or top $-CH_2$ groups and Co–N–H bendings. Due to a considerable $-CH_2$ (rocking displacement)/Co–N–H (bending) interaction, the skew-boat ring shows higher frequencies ν_{31} and ν_{32} than the ring of chair form. The characteristic frequency 959 cm^{-1} of the monohydrate trans complex is quite close to ν_{29} = 953 cm^{-1} or ν_{30} = 949 cm^{-1}, calculated for the skew-boat form. The remaining two peaks of the monohydrate at 896 and 922 cm^{-1} correlate with two of the calculated frequencies among ν_{30}, ν_{31}, and ν_{32} of the chair form. The infrared peaks of the trihydrate trans complex at 890 and 933 cm^{-1} may be assigned to this group of calculated frequencies as well.

Conformational analyses have shown[13-20] that the skew-boat ring contains torsional strains about the C–C bonds, which compensate each other in the ring, so that the ring-puckering potential associated with the rotation around the N- - -N axis of the $-CH_2CH_2CH_2-$ part has a rather flat minimum. It was estimated[14] that a ring-top C atom deviation from the N–Co–N plane of 0.4 Å in the skew-boat ring required a potential energy change of 0.5 kcal/mol. The same increase in the ring strain energy causes a displacement of the ring-top C atom in the chair form of only 0.2 Å. Variations of the dihedral angle of N–Co–N and N–C(side)- - -C(side)–N in the chair ring have also been reported from X-ray studies.[1,10,14,21-26] This change in geometry can be related

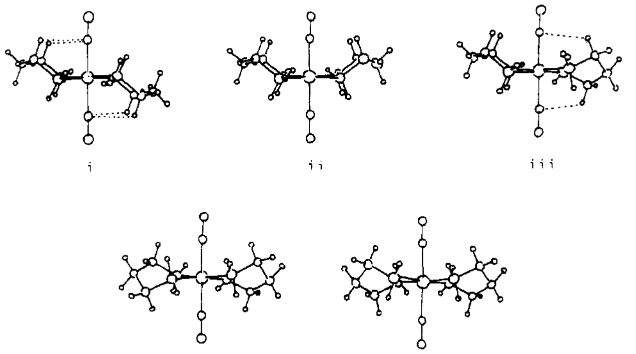

Figure 4. Possible conformational arrangements of *trans*-$[Co(CN)_2(tn)_2]^+$ in solution. Aside from these species, there exist enantiomers of conformers iii and iv and further strained conformers with a ring or rings in a symmetric boat form.

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to the change in frequency. Therefore, calculations of the frequency changes of the distorted ring conformations have been performed by varying the rotation of the $-CH_2CH_2CH_2-$ part (or equivalently of the Co atom) in an interval between 0 to 12° in the skew-boat form and −6 to +6° in the chair form. The coordinates of the hydrogen atoms attached to the nitrogen were obtained by rotation around the Co–N axis by appropriate angles. Results of such calculations are summarized in Table I. It can be seen that some normal modes are found to be rather sensitive to the conformational distortion. However, no considerable frequency change was found upon such distortion for the normal modes of interest.

The conformational analysis indicates further that the chair conformation should be preferred energetically over the skew-boat one. This is due to larger torsional strains around the N–C and C–C bonds in the latter. Moreover, nonbonded interactions between the chelates and the apical ligands in the *trans*-bis(1,3-propanediamine) complexes contribute, even though only in small measure, to the energy difference between chair and skew-boat rings. Hence, the conformers presented in Figure 4 rise energetically in the order i < ii < iii < iv < v, according to the total number of skew-boat rings involved in the complexes. Assuming a Boltzmann distribution, the molar fractions of trans complexes in these particular conformations fall monotonically in the same order. Thus, if in the solution only some fraction of trans complexes containing a skew-boat ring or rings would be present, form iii should be found to be more stable than configurations iv and v, which are much higher in energy. This is apparently not the case; instead, in the case of tris(1,3-propanediamine) complexes the infrared-active vibration at 950 cm^{-1} in the spectra of $[Co(tn)_3]^+$ and $[Cr(tn)_3]^+$ is seen. Since this frequency has been previously attributed to a skew-boat form of the six-membered ring, some fraction of $[M(tn)_3]^{3+}$ (M = Cr, Co) in D_2O seems to have a structure in which the six-membered ring or rings adopt a skew-boat conformation.

Registry No. *trans*-$[Co(NO_3)_2(tn)_2]NO_3$, 22545-85-3; *trans*-$[CoCl_2(tn)_2]Cl$, 31107-58-1; *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$, 103531-52-8; *trans*-$[Co(CN)_2(tn)_2]Cl\cdot 3H_2O$, 103531-53-9; $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$, 52154-76-4; $[Cr(tn)_3]Cl_3$, 17978-78-8; $[Co(tn)_3]Cl_3$, 15242-48-5; D_2, 7782-39-0; tn, 109-76-2; Co, 7440-48-4.

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An Open-Mode Nickel Dimer Based on a Binucleating Hexaphosphine Ligand System. Solid-State and Solution Conformations

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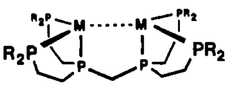
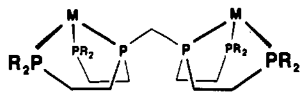
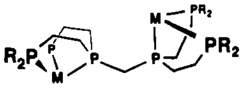
Our interest in exploring the possibilities for dimer systems as homogeneous catalysts have led to the design and synthesis of a hexakis(tertiary phosphine) ligand, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$ (eHTP), which has the ability to both bridge and bis chelate two transition-metal centers in either a closed-mode M–M bonded form (**1a**) or in one of several open-mode conformations (**1b** or **1c**) (assuming that bis chelation will be a driving coordination factor). We have recently reported the synthesis and characterization of the open-mode cobalt dimer $Co_2(CO)_4(eHTP)^{2+}$ (**2**), which has the unique inverted W-shaped eHTP coordination geometry **1b**.[2] We would now like to report two additional variations on the open-mode conformations of eHTP involving nickel(II) eHTP complexes.



1a



1b



1c

Experimental Section

Unless otherwise stated all procedures were carried out under inert atmosphere (prepurified nitrogen or argon) using standard Schlenk line or glovebox techniques. eHTP was prepared according to published procedures.[2] IR spectra were run on a Perkin-Elmer 283B spectrometer. The 300-MHz NMR spectra were performed on a Varian CXP-300 FT spectrometer and referenced to solvent peaks.

Preparation of $Ni_2Cl_2(eHTP)^{2+}(X^-)_2$ (3). A 1.018-g (1.87-mmol) sample of eHTP in 20 mL of degassed EtOH was added dropwise to 0.888 g (3.74 mmol) of $NiCl_2\cdot 6H_2O$ in 20 mL of degassed EtOH under inert atmosphere conditions. The solution rapidly turned from green to dark brown-red. After the addition was complete the solution was stirred for 5 min and vacuum evaporated to dryness to form crude $Ni_2Cl_2(eHTP)^{2+}(Cl^-)_2$ (**3a**) in quantitative yield. **3** is an air-stable solid; solutions, however, slowly react (over several days) with oxygen to give unidentified green solutions. **3a** is soluble in polar organic solvents and water. The crude product was recrystallized by slow evaporation of a 70/20/10 mixture of CH_2Cl_2/toluene/hexane and washed with 3–5 mL of cold CH_2Cl_2 to give red crystals in a yield of 60%.

Crystals of the BF_4^- salt (**3b**) were obtained by adding 0.052 g (0.27 mmol) of $AgBF_4$ (Aldrich) in 5 mL of MeOH to 0.100 g (0.125 mmol) of **3a** in 5 mL of MeOH. A yellow-orange precipitate immediately formed, which was filtered and washed with CH_2Cl_2 to give a clear yellow-orange solution, which was vacuum evaporated to dryness to give an orange-yellow solid. This was dissolved in MeOH and slowly evaporated to yield X-ray quality crystals of **3b**. Crystals of the PF_6^- salt can be obtained by the same procedure using $AgPF_6$.

Satisfactory elemental analyses (Galbraith Laboratories) could not be obtained for **3a** due to the CH_2Cl_2 solvents of crystallization. The BF_4^- salt (**3b**) also did not give satisfactory analyses despite attempts with crystalline samples. ^{31}P NMR for **3a** (CH_2Cl_2 with H_3PO_4 reference): δ 103.8 (pseudo-quintet, 2 P, $J_{P-P} = 30$ Hz), 56.2 (pseudo-doublet, 4 P, $J_{P-P} = 44$ Hz).

X-ray Crystallography for 3a. A well-formed red crystal of **3a** was mounted at the end of a glass fiber with epoxy. A total of 6313 independent reflections were collected at 22 °C on a Nicolet P3 diffractometer using Mo Kα radiation and the $\theta/2\theta$ scan data collection technique with a maximum 2θ angle of 45°. Three standard reflections measured every 100 data points showed no significant change in intensity. Data were corrected for Lorentz and polarization effects, but were not corrected for absorption or extinction. The structure was solved by using the Enraf-Nonius Structure Determination Package via the MULTAN direct-methods programs. The structure was refined by using 5441 reflections with $F_o^2 > 3\sigma(F_o^2)$ to give discrepancy indices of $R = 0.058$ and $R_w = 0.107$ for 388 variables representing 43 anisotropic non-hydrogen atoms. Table I lists information about the data collection and solution, while Tables II and IV list the positional parameters and selected bond distances and angles. Tables of anisotropic thermal parameters and a complete set of bond distances and angles are provided as supplementary material.

van der Waals Energy Calculations. The van der Waals calculations were done on a model system of **3a** derived from the crystallographic coordinates with methyl groups replacing the ethyl groups on the terminal phosphorus atoms. The only geometric parameters varied were rotations (5° increments) about the two $P-CH_2-P$ bonds. No electrostatic factors were included in the energy calculations and both SYBYL and CHEMGRAF program packages gave essentially identical results.

X-ray Crystallography for 3b. A well-formed orange crystal of **3b** was mounted at the end of a glass fiber with epoxy. Mo Kα radiation and the ω-scan data collection technique were used to collect data with a maximum 2θ angle of 45°. Three standard reflections measured every

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