(see above), the geometry at the phosphorus atoms and within the phenyl rings is normal.

There are no unusually short inter- or intramolecular contacts.

Acknowledgments. We are grateful for generous allocations of time on the Univac-1108 computer at The Australian National University Computer Centre.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Large Zero Field Splitting and Subcritical Antiferromagnetic Interactions in $[\mathrm{Ni(C_5H_5NO)_6}](\mathrm{ClO_4})_2$

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Abstract: The single-crystal paramagnetic susceptibilities of $[\mathrm{Ni(C_5H_5NO)_6}](\mathrm{ClO_4})_2$ have been measured between 1.5 and 20 K and indicate a rather large zero field splitting. The data cannot be fit without the inclusion of a significant antiferromagnetic interaction which, however, is of the subcritical kind and which, of itself, cannot lead to long range spin ordering. The resulting parameters are $g_\parallel = 2.32 \pm 0.02$, $g_\perp = 2.33 \pm 0.02$, and $D/k = 6.26 \pm 0.05$ K, with a molecular field constant $zJ/k = -1.5 \pm 0.3$ K.

The nickel(II) ion is a sensitive probe of crystalline field distortions in transition metal complexes.[1] The g value is often isotropic with a value of 2.2–2.3 so, contrary to the case of cobalt, which exhibits widely variable g-value anisotropy,[2] this is not the source of the diagnostic procedure. But, zero field splittings of the ground state may occur, and these vary widely from compound to compound. What is interesting about nickel is that the zero field splittings are typically of the order of a few Kelvins, and thus are easily measured by either susceptibility or specific heat measurements at low temperatures.

The electronic structure of the nickel ion in octahedral fields has been reviewed.[3] A $^3A_{2g}$ ground state is found. Since nickel

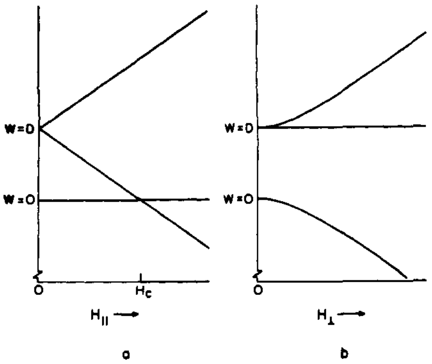

Figure 1. The lowest energy levels of Ni(II) and V(III) in axial crystalline fields as a function of external magnetic field parallel (a) and perpendicular (b) to the principal molecular magnetic axes.

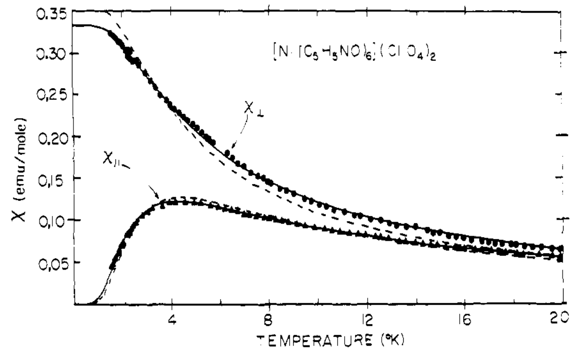

Figure 2. Parallel and perpendicular magnetic susceptibilities of $[Ni(C_5H_5NO)_6](ClO_4)_2$. The points are experimental, and the curves are the best fits to the data with the parameters given in the text. The dashed line omits the molecular field term, and the solid curve includes this term.

is a non-Kramers ion,[4] crystal field effects not only may partially resolve the triple degeneracy of the $^3A_2$ ground state, but may in fact leave a nondegenerate ground state. This is why paramagnetic resonance absorption occasionally does not occur in nickel salts. One such compound, the subject of this paper, is $[Ni(C_5H_5NO)_6](ClO_4)_2$, where C_5H_5NO is pyridine *N*-oxide and, as reported elsewhere,[2] paramagnetic resonance spectra are not observed for this substance even at helium temperatures.

Large crystal field distortions have been observed earlier for both $[Co(C_5H_5NO)_6](ClO_4)_2$[2] and $[Mn(C_5H_5NO)_6](ClO_4)_2$.[5] The static magnetic susceptibilities of the nickel analogue of these molecules have now been examined in order to determine if the lack of EPR spectra is consistent with a large zero field splitting. In fact, it is shown here that $[Ni(C_5H_5NO)_6](ClO_4)_2$ has one of the largest zero field splittings measured directly in a rather simple nickel salt.

The spin-Hamiltonian applicable to trigonally distorted six-coordinate nickel(II) is written as, for $S = 1$,

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + g\mu_B \mathbf{H}\cdot\mathbf{S} \quad (1)$$

where the E term describes rhombic distortions. This parameter may be set equal to zero by symmetry in the present case for $[Ni(C_5H_5NO)_6](ClO_4)_2$ belongs to the rhombohedral crystal system.[6] In zero external field, the first term in eq 1 causes the degenerate $m = \pm 1$ states to separate an amount D in energy from the nondegenerate $m = 0$ state. The parameter D has both sign and magnitude, and is positive if the doubly degenerate levels lie above the singly degenerate one. The situation is illustrated in Figure 1.

Compounds are known that display one sign of D or the other, with, for example, D being positive in $Ni(NO_3)_2 \cdot 6H_2O$[7] and $NiSnCl_6 \cdot 6H_2O$,[8] while D is negative for $NiCl_2 \cdot 4H_2O$[9] and $NiCl_2 \cdot 2py$.[10] This is in contrast to the situation with trivalent vanadium, which likewise has a $^3A_2$ ground state in trigonal fields; to date, all known vanadium(III) compounds have a positive sign for D.[1]

The sign of D (when E is zero) has an important implication for the low temperature properties of nickel salts, in particular, concerning the ability of these salts to undergo long range magnetic ordering. If D is negative, then the ground state always has a nonzero magnetic moment, an exchange interaction, measured by J, among the various ions will occur, and magnetic ordering will set in at some finite temperature, irrespective of the magnitude of D/J. If, however, D has a positive sign, the situation is changed and all the spin entropy can be removed on cooling without the necessary intervention of long-range magnetic ordering processes. This has been discussed on a quantitative basis by Moriya,[11] who shows that a necessary condition for a nonzero critical temperature or Néel point is that D be smaller than $2zJ$, where z is the magnetic lattice coordination number. The situation that pertains to $[Ni(C_5H_5NO)_6](ClO_4)_2$ is shown here to be positive D which is larger than $2zJ$.

Following usual procedures[12] the energy levels and susceptibilities arising from the use of eq 1 may easily be calculated; the susceptibilities are found as

$$\chi_\parallel = (2Ng_\parallel^2\mu_B^2/kT)\exp(-D/kT) \times [1 + 2\exp(-D/kT)]^{-1} \quad (2)$$

$$\chi_\perp = (2Ng_\perp^2\mu_B^2/D)[1 - \exp(-D/kT)] \times [1 + 2\exp(-D/kT)]^{-1} \quad (3)$$

Experimental Section

The compound $[Ni(C_5H_5NO)_6](ClO_4)_2$ is easily prepared by standard procedures[13] and large single crystals may be grown slowly over about a year from DMF solutions. The material is isomorphous to $[Ni(C_5H_5NO)_6](BF_4)_2$ which is[6] rhombohedral with one molecule in the unit cell. Isothermal susceptibilities were measured between 1.5 and 20 K parallel and perpendicular to the hexagonal c axis of the crystals by the mutual inductance procedure. The equipment has been described previously,[9] but of especial significance for the present work is the fact that no external magnetic field is used. On the other hand, the procedure does involve a coil and a small measuring field estimated to be of the order of 5 Oe.

EPR procedures, at X-band, were as earlier.[2] No spectrum was observed below 7 kOe at 4.2, 77, or 300 K.

Results and Discussion

The measured susceptibilities are plotted in Figure 2, along with the best fits (dashed curves) to eq 2 and 3. The resulting parameters are $g_\parallel = 2.23$, $g_\perp = 2.05$, and two values of D/k, 6.81 K (∥) and 9.01 K (⊥). Although these parameters have reasonable values, and suggest that a qualitative description of the data has been obtained, the quantitative analysis is far beyond experimental error. A large nonzero E term is also implied, and therefore this straightforward approach to the problem is rejected. Modification of the equations to include a term due to temperature-independent paramagnetism did not improve the analysis adequately.

A clue to the nature of the situation was provided by the behavior at low temperatures of the isomorphous cobalt compound.[2,14] This salt orders antiferromagnetically at $T_c = 0.42$ K, with an exchange constant of $J/k = -0.21$ K, and is an example of the $S = \frac{1}{2}$, three-dimensional XY model antiferromagnet. Consideration of these facts raised the possibility that rather large but subcritical interactions could also exist among the nickel ions in $[Ni(C_5H_5NO)_6](ClO_4)_2$. If their energy were small enough in comparison with the zero-field splitting of the ground state triplet then no cooperative spin ordering transition would appear above 0 K. This situation has been analyzed in a molecular field approximation.[11,15] In the simple molecular-field picture, the presence of such subcritical interactions would be revealed through their contribution to the effective magnetic field at a nickel ion when an external field was applied. Thus, the single-ion parameters needed to fit the data would be correct only if the interactions were included in the calculation of the susceptibility. These considerations were explored earlier in the magnetic behavior of such salts as $Ni(NO_3)_2{\cdot}6H_2O^7$ and $NiSnCl_6{\cdot}6H_2O^8$ at low temperatures, where it was found necessary to include such exchange effects in order to reconcile the zero-field heat capacity with the near-zero-field magnetic susceptibility.

To include exchange effects, a molecular exchange field is turned on.[9] This field is given by

$$H_i' = \frac{2zJ}{Ng_i^2\mu_B^2}\chi_i' H_i, \qquad i = \parallel, \perp \tag{4}$$

where χ_i' is the exchange-influenced susceptibility actually measured and where the external field H_i and the resulting exchange field H_i' are in the i direction. With this additional field turned on when there is a measuring field, the measured magnetization in the i direction is given by

$$M_i = \chi_i(H_i + H_i') \tag{5}$$

where χ_i is the exchange-corrected susceptibility. Since by definition the measured static susceptibility is given by

$$\chi_i' = \lim_{H_i \to 0} \frac{M_i}{H_i} \tag{6}$$

the exchange-corrected susceptibility is given by

$$\chi_i' = \frac{\chi_i}{1 - (2zJ/Ng_i^2\mu_B^2)\chi_i} \tag{7}$$

Fits of the data using these equations resulted in a substantial improvement in the analysis, as is illustrated by the solid curve in Figure 2. The parameters resulting are $g_\parallel = 2.32 \pm 0.02$, $g_\perp = 2.33 \pm 0.02$, $D/k = 6.26 \pm 0.05$ K, and $zJ/k = -1.5 \pm 0.3$ K. These parameters, with $zJ/k = 0$, do not fit the data satisfactorily. Since the cobalt analogue is a three-dimensional magnet with magnetic coordination number $z = 6$, setting $z = 6$ here leads to $J/k = -0.25$ K. This exchange constant is of the same order of magnitude as that found for the cobalt analogue,[14] though caution must be applied in comparing the numerical values because of the vastly different theoretical procedures used to obtain these parameters.

It has been pointed out[8] that $NiSnCl_6{\cdot}6H_2O$ and its isomorphs are an unusual set of magnetic compounds because there is only one nickel complex per unit cell, with an axial distortion leading to a singlet ground state. The compound $[Ni(C_5H_5NO)_6](ClO_4)_2$ now joins this select group, and may be of more interest because the features that make these compounds interesting and which are now to be described are likely to take place at a higher temperature in the pyridine *N*-oxide compounds than in the hydrate series. Since the *z* axis of all the molecules in these lattices are aligned similarly, an external field can be applied parallel simultaneously to all these *z* axes. As the field increases, as illustrated in Figure 1, one of the higher levels will approach the lower level and they will meet at approximately $g_\parallel\mu_B H_c = D$ or $H_c \sim 40$ kOe in the current case. The significance of this fact is that the ground state will then have (Ising $S' = 1/2$) spin degeneracy which in turn will allow[15] spin ordering to occur at some temperature T_c which, reasoning by analogy with $[Co(C_5H_5NO)_6](ClO_4)_2$,[14] will be of the order of 0.5 K. An elegant demonstration of this phenomenon has already been reported on $Cu(NO_3)_2{\cdot}2.5H_2O$,[16] which is a compound with a spin triplet that is 5.2 K above a spin singlet. In that case, long-range order occurs at 175 mK in an external field of 36 kOe. Experiments such as these are now underway on $[Ni(C_5H_5NO)_6](ClO_4)_2$ in collaboration with the scientists at the Kamerlingh Onnes Laboratorium, Leiden. The salt should also cool upon adiabatic magnetization.[8]

In conclusion, $[Ni(C_5H_5NO)_6](ClO_4)_2$ exhibits a rather large zero field splitting which appears to be unusual in view of the high symmetry of the coordination sphere.[6] The large zero field splitting is consistent with the lack of observation at X-band of the allowed $0 \leftrightarrow \pm 1$ EPR transitions. Large subcritical antiferromagnetic interactions have also been observed which, while they cannot lead to long range magnetic ordering in zero field, suggest that ordering should occur at some low but easily accessible temperature in an external magnetic field.

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Preparation[1a] and Characterization of Chromium(II) Molybdenum(II) Tetraacetate. A Compound Containing a Heteronuclear Quadruple Metal–Metal Bond

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Abstract: The preparation and characterization of the first compound containing a heteronuclear quadruple metal-metal bond, $[\mathrm{CrMo(O_2CCH_3)_4}]$, have been achieved. X-Ray crystallographic studies have shown that this compound is isomorphous with $[\mathrm{Mo_2(O_2CCH_3)_4}]$, with a triclinic unit cell of space group $P\bar{1}$ and dimensions $a = 8.394$ (1) Å, $b = 5.338$ (1) Å, $c = 7.530$ (1) Å, $\alpha = 84.16$ (2)°, $\beta = 103.38$ (2)°, and $\gamma = 105.13$ (2)° with $Z = 1$. The length of the Cr–Mo bond is 2.050 (1) Å. This dimension is consistent with its formulation as a quadruple metal-metal bond and suggests that the typical length of a Cr≣Cr bond is ca. 2.00 Å. The heteronuclear quadruple metal-metal bond appears to be much more labile than related homonuclear bonds and it is readily cleaved under mild conditions.

Although the dimeric metal(II) carboxylates, $[\mathrm{M_2(O_2CR)_2}]$ (where M = Cr,[2-4] Mo,[5-7] Re,[8] Rh,[4,9] or Cu[10]), are well known, remarkably little information has been presented concerning compounds of this or related types containing two different metal atoms. $[\mathrm{MoW(O_2CC(CH_3)_3)_4}]$ has been claimed and $[\mathrm{MoW(O_2CC(CH_3)_3)_4I(CH_3CN)}]$, with a Mo–W bond order of 3.5, characterized.[11] The ions $[\mathrm{CrMoCl_9}]^{3-}$, which may contain strong Cr–Mo interactions, have been synthesized.[12] Here we report the preparation, crystal structure, vibrational spectra, and certain reactions of $[\mathrm{CrMo(O_2CCH_3)_4}]$, the first authenticated example of a quadruple heteronuclear metal-metal bond.

Experimental Section

All manipulations were performed under an atmosphere of purified dinitrogen.

Chromium(II) Molybdenum(II) Tetraacetate. $\mathrm{Mo(CO)_6}$ (1.64 g, 6.2 mmol) was dissolved in a mixture of acetic acid (120 ml), acetic anhydride (20 ml), and dichloromethane (40 ml) and added dropwise over a period of 8 h to a refluxing solution (at 118 °C) of $[\mathrm{Cr_2(O_2CCH_3)_4(H_2O)_2}]$[13] (6.0 g, 16 mmol) dissolved in acetic acid (100 ml) and acetic anhydride (40 ml). The resultant solution was refluxed for a further 16 h, cooled to room temperature, and filtered before the solvent was removed under reduced pressure. A pale yellow precipitate was formed when ca. 150 ml of the solvent remained and this solid was separated by filtration and dried in vacuo to afford $[\mathrm{CrMo(O_2CCH_3)_4}]$ in ca. 30% yield (based on $\mathrm{Mo(CO)_6}$). A pale yellow reasonably air-stable crystalline solid was obtained by sublimation at 170 °C and 10^{-2} Torr. The compound was found to be only sparingly soluble in water and chloroform but reasonably soluble in pyridine where it formed a red solution.

Anal. Calcd for $\mathrm{C_8H_{12}O_8CrMo}$: C, 25.0; H, 3.1; Cr, 13.5; Mo, 25.0. Found: C, 24.6; H, 3.0; Cr, 13.1; Mo, 24.6.

The vibrational spectroscopic data recorded for $[\mathrm{CrMo(O_2CCH_3)_4}]$ are presented in Table I. Ir spectra were recorded on a Perkin-Elmer 225 spectrophotometer and Raman spectra on a Cary 82 instrument using 6328 Å laser excitation. The mass spectrum of the compound was obtained on an A.E.I. MS12 instrument using an electron beam of an energy between 70 and 10 eV. The higher *m/e* values observed in the mass spectrum recorded at this lower energy limit are presented and assigned in Table II.

Carefully controlled sublimation of $[\mathrm{CrMo(O_2CCH_3)_4}]$ at <170 °C and 10^{-2} Torr afforded some of this material as needle-like crystals. Some of these crystals were suitable for x-ray diffraction analysis. Many of them, however, were unsuitable due to various twinning problems, some of which only became apparent on upper layer Weissenberg photographs. Crystal data: $\mathrm{C_8H_{12}O_8CrMo}$; M = 384.1; triclinic; $a = 8.394$ (1), $b = 5.338$ (1), $c = 7.530$ (1) Å; $\alpha = 84.16$ (2), $\beta = 103.38$ (2), $\gamma = 105.13$ (2)°; $U = 315.2$ Å^3, $Z = 1$, $d_c = 2.02$ g cm^{-3}; $F(000) = 190$, Mo Kα radiation, λ 0.7107 Å, μ(Mo Kα) = 19.0 cm^{-1}; space group $P\bar{1}$.

Preliminary unitcell dimensions and space-group data were obtained from Weissenberg, precession, and oscillation photographs and refined on a Hilger and Watts four-circle diffractometer. The layers *hk*0-10 were explored on the diffractometer for a cylindrical shaped crystal ca. 1.5 mm in length and 0.1 mm in cross-sectional diameter, and 1349 reflections with $I > 3\sigma(I)$ in the range $0 < 2\theta < 62°$ were considered observed and used in the subsequent refinement. No account was taken of anomalous dispersion, and no corrections were made for secondary extinction or absorption; the maximum error introduced by the neglect of absorption effects was estimated to be ca. 10% in *F*. Data reduction and crystallographic calculations were carried out on the Nottingham University I.C.L. 1906A computer using the Oxford University "CRYSTALS" programs. Atomic scattering factors were used as published.[14] The positions of the metal atoms were located from a three-dimensional Patterson synthesis, and a three-dimensional Fourier synthesis in $P\bar{1}$ symmetry, with molybdenum atoms on both the metal sites, revealed the positions of the two acetato groups in the asymmetric unit. Refinement was then continued in the expected $P1$ symmetry using least-squares procedures and this converged[15] at $R_1 = 0.11$. This level of refinement was considered to be unsatisfactory and further refinement was then attempted in $P\bar{1}$ symmetry, each metal site being occupied by 0.5 Cr and 0.5 Mo atoms. This approach resulted in a significant improvement in the refinement, the final R_1 and R_2 values being 0.053 and 0.067, respectively. In the final difference Fourier the highest peaks were of ca. 1 eÅ^{-3} in density and were in the vicinity of the metal atoms; several peaks of density ca. 0.5 eÅ^{-3} were in positions in which the hydrogen atom would be expected and therefore it was not considered worthwhile to attempt to locate these latter atoms.

The final atomic coordinates and thermal parameters are listed in Table III, the relevant interatomic distances and interbond angles in Table IV, and the important least-squares planes are defined in Table V. A table of structure factors is available.[16]

Reactions of Chromium(II) Molybdenum(II) Tetraacetate. A. $[\mathrm{CrMo(O_2CCH_3)_4}]$ (0.48 g, 1.28 mmol) was stirred with a mixture of $\mathrm{CF_3CO_2H}$ (5 ml) and $\mathrm{(CF_3CO)_2O}$ (0.5 ml) at ca. 25 °C for 16 h. A small amount of a pale green solid ($[\mathrm{Cr(O_2CCF_3)_3}]$?) was removed by filtration and the subsequent removal of solvent in vacuo yielded a bright yellow solid which was purified by sublimation (80 °C, 10^{-2} Torr) to give a bright yellow crystalline solid. The analytical data obtained for this solid Cr 5.0% Mo 21.6% was consistent with a mixture of $[\mathrm{CrMo(O_2CCF_3)_4}]$ and $[\mathrm{Mo_2(O_2CCF_3)_4}]$ in the molar ratio 4:3. The mass spectrum of this material contained, in addition to peaks at *m/e* values characteristic of $[\mathrm{Mo_2(O_2CCF_3)_4}]$, peaks at the following *m/e* values (for ^{96}Mo) (of the approximate relative intensity) which are tentatively assigned as follows: 600 (8) $[\mathrm{CrMo(O_2CCF_3)_4}]^+$, 546 (55) $[\mathrm{CrMo(O_2CCF_3)_3(OCCF)}]^+$, 527 (21) $[\mathrm{CrMo(O_2CCF_3)_3(OC_2)}]^+$, 506 (11) $[\mathrm{CrMo(O_2CCF_3)_3F}]^+$, 492 (69) $[\mathrm{CrMo(O_2CCF_3)_2(OCCF_2)(OC_2)}]^+$, 452 (75) [CrMo-