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Syntheses and Magnetic Properties of 1,4,8,11-Tetraazacyclotetradecanenickel(II) Tetra-, Hexa-, and Octacyanometalates

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A series of 1,4,8,11-tetraazacyclotetradecanenickel(II) cyanometalates ($[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ (**1**), $[Ni(cyclam)]_2[Mo(CN)_8]\cdot 3H_2O$ (**2**), $[Ni(cyclam)]_2[W(CN)_8]\cdot 3H_2O$ (**3**), and $[Ni(cyclam)][Pt(CN)_4]\cdot 3H_2O$ (**4**) (cyclam = 1,4,8,11-tetraazacyclotetradecane)) was obtained and characterised. Magnetic-susceptibility measurements showed a high-spin configuration (S = 1) of Ni(II) in all compounds, which was attributed to the interaction of cyano ligands with free axial coordination sites on nickel. The presence of bridging cyano groups in **1** was confirmed by IR and visible reflectance spectra. Compound **1** shows a long-range magnetic order below 8 K.

Research into molecular-based magnetic materials is a rapidly developing branch of modern solid state science. Interest in this field started with the first reports of co-operative magnetism in molecular solids: the discovery of metamagnetic $[Fe(Cp^*)_2][tcnq]$ in 1979[1)] and ferromagnetic $[Fe(Cp^*)_2][tcne]$ in 1986[2)] (Cp* = pentamethylcyclopentadienyl, tcnq = tetracyanoquinodimethane, tcne = tetracyanoethylene). Magnets composed of molecular species have several advantages over traditional metallic magnets, which make them desirable industrial materials. They can potentially combine magnetic with other properties (optical, electrical and mechanical), and they are prepared by relatively easy and low-temperature synthesis, as compared to metallurgical processes. It is generally considered that bulk ferromagnetic properties require the alignment of spins in all three directions.[3—5)] Quite often, however, molecular solids with the magnetic order restricted to one[6—10)] or two[11,12)] dimensions exhibit magnetic properties at low temperatures. In such compounds the ferro- or ferrimagnetic interactions spread within separate chains (1D) or planes (2D). Low-dimensional magnets are valuable model systems, which can give some insight into the nature of cooperative magnetism in molecular solids.

Most molecular magnetic materials belong to one of two classes of compounds. The first one includes charge-transfer salts consisting of an organic radical ion and metal complex.[1—3,9,13)] To this class belongs the room-temperature ferromagnet $[V(tcne)_2]\cdot 0.5CH_2Cl_2$.[3)] The second group comprises bimetalic compounds,[14)] where two different metals (or the same metal in two different environments) form stacks[15)] or polymeric structures connected by bridging ligands.[4—8,10—12,16)] Cyano ligands, due to their good bridging properties, are often encountered in the latter structures. The dimensionality of cyano-bridged polymers can be easily controlled by blocking a different number of coordination sites with chelate ligands or the choice of stoichiometry.[4,5,8,10—12,16,17)]

Nickel(II) complexes of cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) and related tetradentate macrocycles have been successfully used in the synthesis of magnetic materials.[6,12,18)] Salts of $[Ni(cyclam)]^{2+}$ with non-coordinating anions, like perchlorate, are diamagnetic (S = 0). However, the square-planar complex easily binds coordinating anions (halides) or solvent molecules (dmso, MeCN), giving octahedral structures.[19—21)] Enhanced symmetry results in a high-spin configuration (S = 1) and paramagnetic properties of the compounds. Our aim was to study the interaction of 1,4,8,11-tetraazacyclotetradecanenickel(II) with cyano complexes of different coordination numbers. We have chosen tetracyanoplatinate(II), octacyanomolybdate(IV) and -tungstate(IV), and hexacyanoferrate(III).

Results and Discussion

Synthesis and Properties of the Compounds. The addition of $[Ni(cyclam)](ClO_4)_2$ to a solution of $K_3[Fe(CN)_6]$, $K_4[Mo(CN)_8]\cdot 2H_2O$, $K_4[W(CN)_8]\cdot 2H_2O$ or $K_2[Pt(CN)_4]$ causes immediate precipitation of the respective 1,4,8,11-tetraazacyclotetradecanenickel(II) cyanometalate. The compounds of the formulae ($[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ (**1**), $[Ni(cyclam)]_2[Mo(CN)_8]\cdot 3H_2O$ (**2**), $[Ni(cyclam)]_2[W(CN)_8]\cdot 3H_2O$ (**3**), and $[Ni(cyclam)][Pt(CN)_4]\cdot 3H_2O$ (**4**)) have been isolated as powders. Compounds **2**, **3** and **4** are yellow, as the substrates used for their synthesis, while brown

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1 differs in colour from [Ni(cyclam)]$(ClO_4)_2$ and $K_3[Fe(CN)_6]$, which are both yellow. All salts are stable in air at room temperature. With increased temperature, the water of crystallisation is released. Anhydrous compounds can be obtained by thermal dehydration at 80 °C. In the case of **1** and **4**, the loss of water is accompanied by a colour change from brown to brownish green and from yellow to cream, respectively. Left in air, the anhydrous salts are rehydrated to their original composition. The process is fastest for the iron (**1**) and slowest for the platinum (**4**) compound. Reversible dehydration at relatively low temperature indicates a very weak interaction of water molecules with complex ions. All compounds are practically insoluble in common solvents, suggesting a polymeric structure.

Magnetic-susceptibility measurements at room temperature show that all compounds are paramagnetic. The effective magnetic moments ($\chi_m T$) are equal to 5.1 (**1**), 2.0 (**2**), 2.1 (**3**), and 0.8 $cm^3\,K\,mol^{-1}$ (**4**). The same values were obtained for hydrated and anhydrous salts. Since $[Fe(CN)_6]^{3-}$ is in a low-spin state ($S = 1/2$) and the other cyanometalates are diamagnetic, the $[Ni(cyclam)]^{2+}$ component should have a high-spin configuration ($S = 1$). With $g_{Fe} = g_{Ni} = 2$, the theoretical $\chi_m T$ values of spin-diluted systems are obtained as 3.75 (**1**), 2.00 (**2** and **3**) and 1.00 $cm^3\,K\,mol^{-1}$ (**4**). The last three are in reasonable agreement with the experimental values. The reason why the $\chi_m T$ value of **1** is higher than expected will be discussed later. The results confirm that nickel(II) in all salts has a high-spin configuration. The transition of diamagnetic $[Ni(cyclam)]^{2+}$ to the high-spin state is usually caused by a change of square-planar to octahedral geometry through the incorporation of two ligands in axial positions.[19—21] In the studied systems this can be achieved by coordination via the nitrogen atoms of cyano ligands or by water molecules. The latter case can be excluded, because the magnetic susceptibility does not change upon dehydration. Therefore, we can assume the formation of CN bridging groups.

Spectra. The IR spectrum of compound **1** (Fig. 1) contains three C≡N stretching bands at 2110, 2146 and 2159 cm^{-1}, in comparison to only one band at 2115 cm^{-1} for $K_3[Fe(CN)_6]$, which confirms the presence of bridging cyano groups. In the spectra of **2** and **3** three strong bands are present in the region of 2085—2124 cm^{-1}. Since octacyanides usually exhibit several ν(C≡N) bands, depending on the symmetry,[22] no firm conclusion can be drawn in these cases. Similarly, only two very close bands at 2128 and 2133 cm^{-1} are observed for **4**. Compared with the two bands at 2122 and 2133 cm^{-1} for $K_2[Pt(CN)_4]$, they give no clear evidence for CN bridges. There are, however, several examples of cyano-bridged compounds, where very little or no shift of ν(C≡N) bands have been observed.[23]

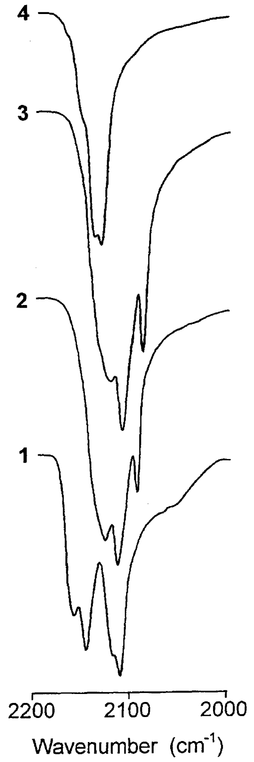

Fig. 1. IR spectra (%T) of $[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ (**1**), $[Ni(cyclam)]_2[Mo(CN)_8]\cdot 3H_2O$ (**2**), $[Ni(cyclam)]_2[W(CN)_8]\cdot 3H_2O$ (**3**), and $[Ni(cyclam)][Pt(CN)_4]\cdot 3H_2O$ (**4**) in C≡N stretching region.

The diffuse reflectance spectrum of **1** (Fig. 2) shows the presence of a broad asymmetric absorption from 600 nm to the near-infrared region. In the sequence **2**, **3**, **4** the corresponding broad absorption gradually develops into two separated bands. [Ni(cyclam)]$(ClO_4)_2$ and potassium cyanometalates do not absorb in that region; therefore, the new bands result from interactions between ions. By comparison with the diffuse reflectance spectrum of [Ni(cyclam)Br_2], which shows a broad asymmetric band in the range from 700 to 900 nm,[19] we tentatively assigned the new bands in **1**—**4** to ligand field transitions of the octahedrally distorted nickel component. The appearance of these bands, therefore, corroborates the presence of bridging cyano groups also for these complexes.

Magnetic Properties of $[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ (1). The magnetic susceptibilities of **1**—**4** were measured in the temperature range from 1.7 to 300 K with an applied field of 0.1 T. The results were corrected for diamagnetism[24] and the temperature-independent paramagnetism of Ni(II).[25] The temperature dependence of the magnetic susceptibility for compound **1** is presented in Fig. 3 in the form of a $\chi_m T$ vs. temperature plot. The $\chi_m T$ at room temperature (5.13 $cm^3\,K\,mol^{-1}$) is higher than naively expected for the spin-diluted $S = 3\times 1(Ni) + 2\times 1/2(Fe)$ system (3.75 $cm^3\,K\,mol^{-1}$ with $g_{Fe} = g_{Ni} = 2$). Since the $\chi_m T$ values of 1.90—2.25 were measured for $K_3[Fe(CN)_6]$,[26] while the theoretical value is 1.73, we take the highest value (2.25) of $\chi_m T$ of $[Fe(CN)_6]^{3-}$ in compound **1**. Then, from the observed $\chi_m T$, the g value for Ni^{2+} is evaluated to be 2.27, which is generally accepted for nickel(II) in an octahedral ligand field. High $\chi_m T$ values at room temperature were also observed for similar cyano bridged compounds.[10,11,17] With decreasing temperature, $\chi_m T$ remains constant down to about 50 K, then increases, reaching a maximum of 29 $cm^3\,K\,mol^{-1}$ at

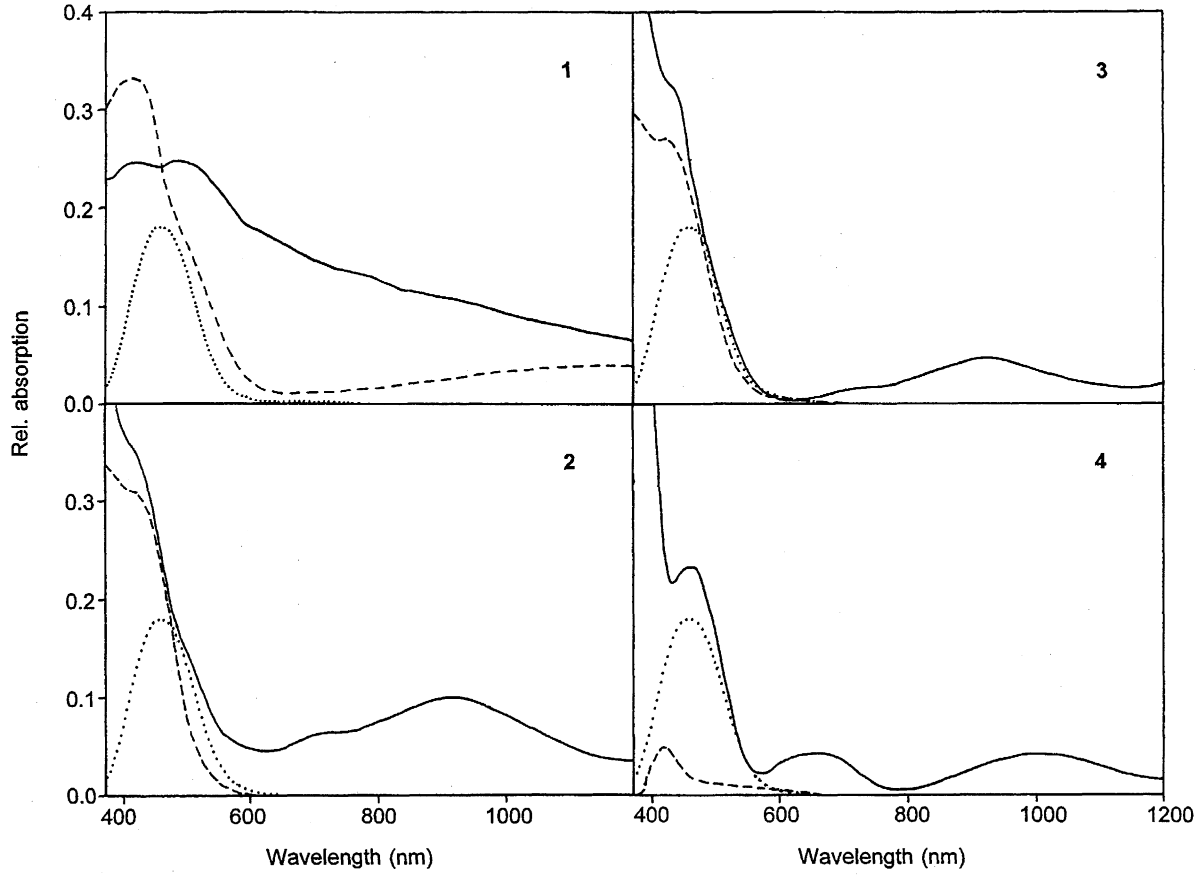

Fig. 2. Diffuse reflectance spectra of $[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 11H_2O$ (**1**), $[Ni(cyclam)]_2[Mo(CN)_8] \cdot 3H_2O$ (**2**), $[Ni(cyclam)]_2[W(CN)_8] \cdot 3H_2O$ (**3**), and $[Ni(cyclam)][Pt(CN)_4] \cdot 3H_2O$ (**4**) (solid lines) in comparison to corresponding potassium cyanometalate (broken lines) and $[Ni(cyclam)](ClO_4)_2$ (dotted lines).

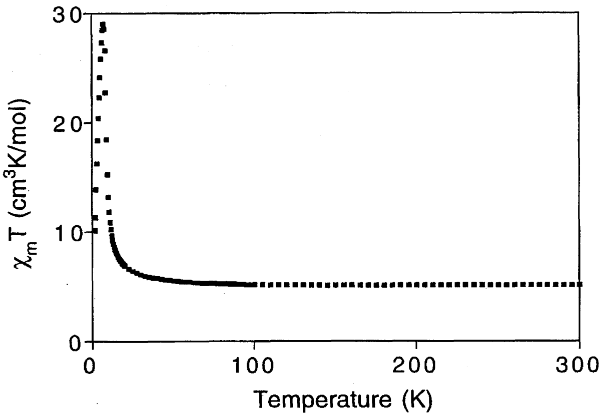

Fig. 3. Temperature dependence of $\chi_m T$ for $[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 11H_2O$ (**1**) at applied field of 0.1 T.

8 K, and below that rapidly drops down. The initial increase of $\chi_m T$ suggests the presence of ferromagnetic coupling between magnetic sites, most likely across the CN bridges. The steep drop below 8 K implies that long-range ordering occurs at 8 K. The ferromagnetic coupling between the metal ions through CN bridges is rationalised by the orthogonality of partially occupied (magnetic) orbitals of Ni (e_g) and Fe (t_{2g}). The results of field-cooled (FC) and zero-field cooled (ZFC) magnetisation measurements are shown in Fig. 4. In the FC experiment the susceptibility grows rapidly below 10 K, and the slope breaks at 8 K, tending to saturation at low temperatures. The ZFC susceptibility reaches maximum at around

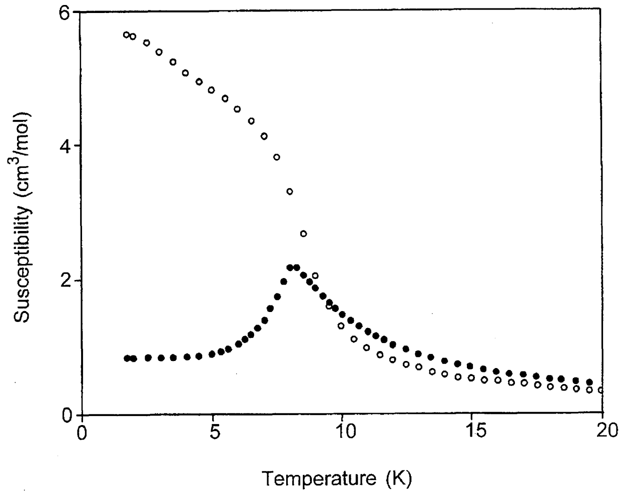

Fig. 4. Temperature dependence of magnetic susceptibility χ_m of $[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 11H_2O$ (**1**) in field cooled (fool circles) and zero field cooled (empty circles) measurements.

8 K, and then decreases, which is characteristic of polycrystalline ferromagnets. The magnetisation measurements were performed at 4.5 and 2 K (Fig. 5). The small hysteresis (below 0.1 T) observed at 4.5 K became larger (about 0.5 T) at 2 K, proving that **1** is a soft ferromagnet at liquid-helium temperatures. The magnetisation is not saturated even at 1 T. It is probably connected with the presence of a number of magnetic domains of different sizes distributed in the sample. The interdomain interactions may be antiferromagnetic, because of the large difference between the zero-field and field-cooled susceptibilities.

The magnetic susceptibilities of compounds **2**—**4** show no anomalous behaviour. The $\chi_m T$ values remain constant at high temperatures and decrease rapidly below 15 K. Compounds **2** and **3** have the $\chi_m T$ values of about 1.1 $cm^3 K mol^{-1}$ per one mol of Ni(II), while $\chi_m T$ of **4** is only 0.75. This discrepancy remains unclear.

Conclusions. We have obtained four 1,4,8,11-tetraazacyclotetradecanenickel(II) cyanometalates. The physical properties of the compounds (insolubility, magnetic susceptibility, low temperature dehydration, and reflectance spectra) indicate that they have a polymeric structure, although no proof of cyano-bridging was found in the IR spectra of **2**, **3**, and **4**. Compound **1** shows a long-range magnetic order with a critical temperature of 8 K. A similar low-temperature magnetic behavior was observed for related Ni(II)–Fe(III)[11] and Ni(II)–Cr(III)[12] assemblies.

Experimental

[Ni(cyclam)]$(ClO_4)_2$[19] and $K_4[M(CN)_8]\cdot 2H_2O$ (M = Mo, W)[27] complexes were prepared according to published methods. Other reagents and solvents of analytical grade were used as supplied.

Syntheses. $[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ **1**: Aqueous solutions of $K_3[Fe(CN)_6]$ (20 ml, 0.4 mmol, 0.13 g) and [Ni(cyclam)]$(ClO_4)_2$ (90 ml, 0.6 mmol, 0.27 g) were heated to 60 °C, then mixed together and kept at 50 °C with stirring for 2 h. The resulting precipitate was filtered off, washed several times with water and dried under air. Brown powder (0.21 g, 74%). Found: C, 36.14; H, 6.78; N, 24.12%. Calcd for $C_{42}H_{94}N_{24}O_{11}Ni_3Fe_2$: C, 36.06; H, 6.77; N, 24.03%. IR 880m, 959s, 1006w, 1060w, 1097vs, 1240vw, 1291w, 2115vs, 2146s, 2161m.

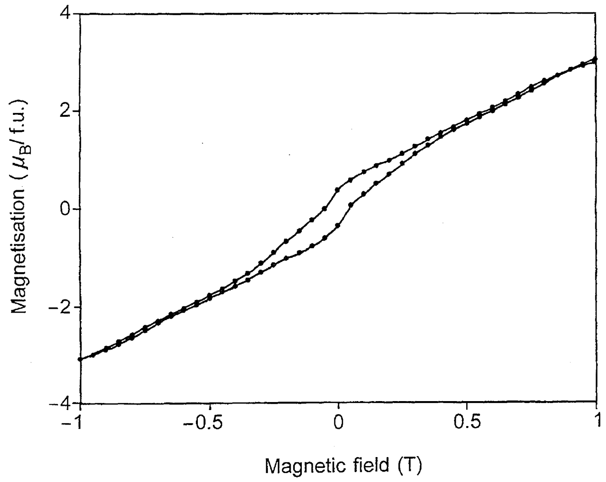

Fig. 5. Magnetisation of $[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 11H_2O$ (**1**) at 2 K.

$[Ni(cyclam)]_2[Mo(CN)_8]\cdot 3H_2O$ **2** was prepared analogous to compound **1** using $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.3 mmol, 0.15 g). Yellow powder (0.16 g, 61%). Found: C, 37.99; H, 6.26; N, 25.40%. Calcd for $C_{28}H_{54}N_{16}O_3Ni_2Mo$: C, 38.38; H, 6.21; N, 25.58%. IR 880w, 965m, 1006w, 1062w, 1100vs, 1242vw, 1291vw, 2090s, 2110vs, 2124vs.

$[Ni(cyclam)]_2[W(CN)_8]\cdot 3H_2O$ **3** was prepared analogous to compound **1** using $K_4[W(CN)_8]\cdot 2H_2O$ (0.3 mmol, 0.18 g). Yellow powder (0.16 g, 55%). Found: C, 34.60; H, 5.64; N, 22.98%. Calcd for $C_{28}H_{54}N_{16}O_3Ni_2W$: C, 34.88; H, 5.65; N, 23.25%. IR 880w, 963m, 1008w, 1061w, 1099s, 1242vw, 1291vw, 2085s, 2106vs, 2122s.

$[Ni(cyclam)][Pt(CN)_4]\cdot 3H_2O$ **4**: An aqueous solution (20 ml) of $K_2[Pt(CN)_4]$ (0.3 mmol, 0.13 g) was mixed with an aqueous solution (50 ml) of [Ni(cyclam)]$(ClO_4)_2$ (0.3 mmol, 0.14 g) and the resulting precipitate was filtered off, washed several times with water and dried under air. Yellow powder (0.16 g; 87%). Found: C, 27.53; H, 5.00; N, 18.3%. Calcd for $C_{14}H_{30}N_8O_3NiPt$: C, 27.47; H, 4.94; N, 18.30%. IR 880w, 970w, 982w, 1014w, 1066vw, 1098m, 1114w, 1294vw, 2128vs, 2133vs.

The anhydrous salts were obtained by thermal dehydration of **1**—**4** at 80 °C for about 2 h.

Analytical Methods and Physical Measurements. Carbon, nitrogen, and hydrogen were determined by organic microanalysis on a Carlo Erba Elemental Analyser 1106. The water content was determined by thermal dehydration at 80 °C to constant weight. Infrared spectra were measured as nujol mulls on a Perkin–Elmer 16PC FT-IR spectrometer. UV-vis-NIR (NIR = near infrared) diffuse reflectance spectra were recorded on a Shimadzu 3101 PC spectrometer. The magnetic susceptibility at room temperature was measured on a Johnson Matthey magnetic-susceptibility balance. The temperature dependence of the magnetic susceptibility was measured with a Quantum Design MPMS2 SQUID magnetometer in the temperature range 1.7 to 300 K with an applied field of 0.1 T. Experimental susceptibility data were corrected for diamagnetism using Pascal's constants.[24]

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