

**METAL PSEUDOHALIDE COMPLEXES. XVII**  
**ANTIFERROMAGNETIC INTERACTIONS IN SOME NICKEL(II) AZIDE**  
**DIMERS WITH PYRIDINE LIGANDS**

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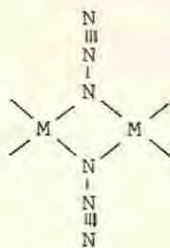
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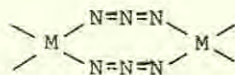
**ABSTRACT.** The magnetic susceptibilities of  $Ni(4-Etpy)_4(N_3)_2$  and  $NiL_2(N_3)_2$  complexes, where L = 4-bromo-, 4-acetyl-, and 4-cyano-pyridine, have been measured between 80 and 300 K. These data are treated on the basis of the Curie-Weiss law and two other theoretical expressions. The calculations show that  $NiL_2(N_3)_2$  dimers exhibit antiferromagnetic interactions with the singlet-triplet gap J from  $-0.31$  to  $-37.5$  cm<sup>-1</sup>.

**INTRODUCTION**

It is well known that azide ion may coordinate a metal ion via one of its end nitrogen atoms and thus act as a terminal group (1). Alternatively, it can bridge two metal atoms through one nitrogen giving rise to four membered ring (A) or link two metal atoms via two nitrogens giving eight-membered ring (B).



(A)



(B)

It is also well known that the azide stretching mode becomes infrared active in mode (A) and remains IR-inactive in mode (B). That  $\nu_s(N_3^-)$  remains inactive in end-to-end azide complexes was assumed on the basis that the two N-N distances in this case are almost of equal length, i.e. the azide group is symmetrical. However, in many cases, terminal azides were found to be symmetric as in  $Fe(N_3)_5^{2-}$  (2) (i.e. the  $\nu_s(N_3^-)$  is IR-inactive) which in others end-to-end azides are asymmetric (e.g. in  $[Cu(tmen)(N_3)_2]$  (tmen = N,N,N',N'-tetramethylethylenediamine) (3) and hence the  $\nu_s(N_3^-)$  mode is IR-active. Moreover, in some cases where there is the possibility of two types of azide, it is difficult to conclude the mode of bonding of the azide groups unambiguously on the basis

of infrared spectral results alone. Only in case where the azide groups are bonded in the same fashion (as in  $\text{Cd}(\text{py})_2(\text{N}_3)_2$ ) (4) is the infrared spectrum valuable.

It was pointed out (5) that when  $\text{N}_3^-$  bridges in mode (A), then ferromagnetic interaction is favoured (6,7), whereas mode (B) leads to strongly antiferromagnetic interactions (8,9). For the asymmetrical bridging azide in (B) the interaction is either negligible or weakly antiferromagnetic depending on the stereochemistry around the metal atom (10,11). In this paper, the magnetic susceptibilities of some nickel(II) azide complexes, which have been prepared previously (12), are reported.

## EXPERIMENTAL

Syntheses of the complexes and their physical characterization (elemental analysis, infrared and electronic spectra) were done as previously described (12).

The magnetic susceptibilities from 80 to 300 K were measured by Gouy's method.  $\text{HgCo}(\text{NCS})_4$  was used as a calibrant and the samples were measured at 1 and 2 kilogauss. Pascals units were used for diamagnetic corrections.

Least-squares fitting of the magnetic susceptibility curves was carried out on an IBM PC/XT computer with SPSS/PC statistical package for the Curie-Weiss law. A special program was written to perform non-linear square analysis using the grid search method for other fitting equations. The simple method (10) was used for minimization. The function minimized was:

$$\Delta = \sum_i^{NP} \{ [\chi_M^{\text{obsd}}]_i - \chi_M^{\text{calc}} \}^2 T^N$$

where NP is the number of experimental points and N can be adjusted to emphasize selectively the regions of the susceptibility curve which could be fit most closely. Generally, fits to equation 3 were with  $N = 0$ .

The goodness of fit, or standard error of estimate SE, was estimated from the expression suggested by Ginsberg (11).

$$SE = \left\{ \sum_{i=1}^{NP} [ \mu_{\text{eff}}^{\text{obsd}}]_i - \mu_{\text{eff}}^{\text{calc}} \right\}^2 / (NP - K)^{\frac{1}{2}}$$

in this expression K is the number of parameters used to fit the NP data points.

## RESULTS AND DISCUSSION

The magnetic susceptibilities of some azido-nickel(II) complexes, namely  $\text{Ni}(4\text{-Etpy})_4(\text{N}_3)_2$ ,  $\text{Ni}(4\text{-Brpy})_2(\text{N}_3)_2$ ,  $\text{Ni}(4\text{-Acpy})_2(\text{N}_3)_2$  and  $\text{Ni}(4\text{-Cypy})_2(\text{N}_3)_2$ , where 4-Etpy = 4-ethylpyridine, 4-Brpy = 4-bromopyridine, 4-Acpy = 4-acetylpyridine and 4-Cypy = 4-cyanopyridine, were measured from 80 to 300 K.

The magnetic data were analysed on the assumption that the complexes obey the Curie-Weiss law:  $\chi_M^{\text{corr}} = C(T - \theta)^{-1}$ . The Curie and Weiss constants C and  $\theta$ , respectively, were calculated by a standard linear least-squares method. The results of such calculations are given in Tables 1-4 and Figures 1 & 2.



Table (1). Variable temperature magnetic data for  $\text{Ni(4-Etpy)}_4(\text{N}_3)_2$  (calculated values are given according to the Curie-Weiss law).

T K	$\chi_g \times 10^6$	$\chi_M \times 10^3$		$\mu_{\text{eff}} \text{ (BM)}$	
	cgsu	Exp.	Calc.	Exp.	Calc.
85	41.25	23.9	28.1	4.03	4.37
110	26.93	15.7	16.4	3.72	3.81
135	20.27	11.9	11.6	3.59	3.54
160	16.03	9.4	9.0	3.49	3.39
185	13.02	7.76	7.33	3.39	3.29
220	10.27	6.19	5.82	3.30	3.20
250	7.33	4.51	4.95	3.01	3.15
300	6.44	4.00	3.96	3.10	3.08

Diamagnetic correction =  $324.88 \times 10^{-6}$  cgsu/mol.

$$C = 0.9909 \pm 0.0527$$

$$\theta = 49.7 \pm 2.3 \text{ K}$$

Table (2). Variable temperature magnetic data of  $\text{Ni(4-Brpy)}_2(\text{N}_3)_2$ . [calculated values are given according to Curie-Weiss equation, equation (1) and equation (2)].

T K	$\chi_M \times 10^3 \text{ (cgsu)}$				$\mu_{\text{eff}} \text{ (BM)}$			
	Exp.	Calculated			Exp.	Calculated		
		Curie-Weiss	Eqn. 1	Eqn. 2		Curie-Weiss	Eqn. 1	Eqn. 2
80	12.305	12.393	12.126	12.007	2.81	2.82	2.79	2.77
120	9.859	10.088	10.248	10.441	3.08	3.11	3.14	3.17
150	8.853	8.853	8.979	9.095	3.25	3.26	3.28	3.31
180	7.988	7.887	7.930	7.948	3.39	3.37	3.38	3.38
220	7.107	6.885	6.823	6.741	3.54	3.48	3.47	3.45
260	6.245	6.110	5.969	5.824	3.61	3.57	3.53	3.48
300	5.323	5.491	5.297	5.114	3.58	3.63	3.58	3.51

Diamagnetic correction =  $-180.16 \times 10^{-6}$  cgsu/mol.,  $N\alpha = 200 \times 10^{-6}$  cgsu.

Curie-Weiss equation	Eqn. 1	Eqn. 2
$\theta = -95.0 \pm 1.0 \text{ K}$	$J = -34.4 \text{ cm}^{-1}$	$J = -34.9 \text{ cm}^{-1}$
$C = 2.17 \pm 0.10$	$\theta = 12.1 \text{ K}$	$Z'J' = 17.1 \text{ K}$
	$g = 2.689$	$g = 2.523$
	$SE = 0.0163$	$D = 0.004 \text{ cm}^{-1}$
		$SE = 0.0433$

Table (3). Variable temperature magnetic data of  $Ni(4-Cypp)_2(N_3)_2$  [calculated values are given according to Curie-Weiss equation, equation (1) and (2)].

T K	$\chi_M \times 10^3$ (cgsu)				$\mu_{eff}$ (BM)			
	Exp.	Calculated			Exp.	Calculated		
		Curie-Weiss	Eqn. 1	Eqn. 2		Curie-Weiss	Eqn. 1	Eqn. 2
80	17.029	17.493	17.029	17.009	3.30	3.35	3.30	3.30
120	11.351	11.495	11.398	11.429	3.30	3.32	3.31	3.31
160	8.607	8.560	8.567	8.578	3.32	3.31	3.31	3.32
200	6.926	6.819	6.863	6.859	3.33	3.30	3.32	3.31
250	5.574	5.436	5.498	5.483	3.34	3.30	3.32	3.31
300	4.425	4.521	4.586	4.566	3.26	3.30	3.32	3.31

Diamagnetic correction =  $-135.24 \times 10^{-6}$  cgsu/mol.,  $N_A = 200 \times 10^{-6}$  cgsu.

Curie-Weiss	Eqn. 1	Eqn. 2
$\theta = 3.3 \pm 8.7$ K	$J = -0.6 \text{ cm}^{-1}$	$J = -9.2 \text{ cm}^{-1}$
$C = 1.3 \pm 0.04$	$\theta = -0.04$ K	$Z'J' = 5.8$ K
	$g = 2.346$	$g = 2.328$
	SE = 0.0043	SE = 0.0039

Table (4). Variable temperature magnetic data of  $Ni(4-Acyp)_2(N_3)_2$  [calculated values are given according to Curie-Weiss equation, equation (1) and equation (2)].

T K	$\chi_M \times 10^3$ (cgsu)				$\mu_{eff}$ (BM)			
	Exp.	Calculated			Exp.	Calculated		
		Curie-Weiss	Eqn. 1	Eqn. 2		Curie-Weiss	Eqn. 1	Eqn. 2
80	6.731	6.502	6.541	6.528	2.08	2.04	2.05	2.05
120	5.052	5.115	5.175	5.182	2.20	2.21	2.23	2.23
150	4.338	4.410	4.478	4.488	2.28	2.30	2.32	3.32
200	3.536	3.586	3.660	3.670	2.38	2.39	2.42	3.42
250	3.066	3.021	3.096	3.104	2.48	2.45	2.49	2.49

Diamagnetic correction =  $-172.28 \times 10^{-6}$  cgsu/mol.,  $N_A = 200 \times 10^{-6}$  cgsu.

Curie-Weiss	Eqn. 1	Eqn. 2
$\theta = -67.5 \pm 1.4$ K	$J = -0.26 \text{ cm}^{-1}$	$J = -2.3 \text{ cm}^{-1}$
$C = 0.96 \pm 0.02$	$\theta = -72.9$ K	$Z'J' = -26.4$ K
	$g = 2.000$	$g = 2.000$
	SE = 0.0051	D = 0.002 $\text{cm}^{-1}$
		SE = 0.0051

As seen from Table 1 and Fig. 1, the magnetic susceptibility data of the tetrakis-(4-ethylpyridine)nickel(II) azide complex obeys the Curie-Weiss law in the 80-300 K range, as confirmed by  $1/\chi_M$  vs T plots which are linear (cf. Fig. 2). However, the calculated  $\theta$  value of +49.7 K indicates strong magnetic interactions and hence the compound is magnetically concentrated. This result contrasts the stoichiometry as well as the electronic spectrum of the compound. The spectrum exhibits a band at 640 nm due to  $\nu_2$ ,  ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ , transition (12), suggesting an octahedral structure. The high value of  $\theta$  is therefore unexpected. In fact, all other pyridine derivatives form only 2:1 complexes with nickel(II) azide. Moreover, the carbon content of this compound was found to be lower than the calculated value. Possibly, the strong magnetic interaction is due to a large contamination of the *tetrakis* complex by a *bis*-(Etpy) complex.

Fig. 1. Paramagnetic susceptibility data (cgsu/mole) vs temperature for  $\text{Ni}(4\text{-Etpy})_4(\text{N}_3)_2$ ; ( $\ast$ ) calculated  $\chi_M$  values (according to Curie-Weiss equation),  $\circ$  experimental  $\chi_M$ .

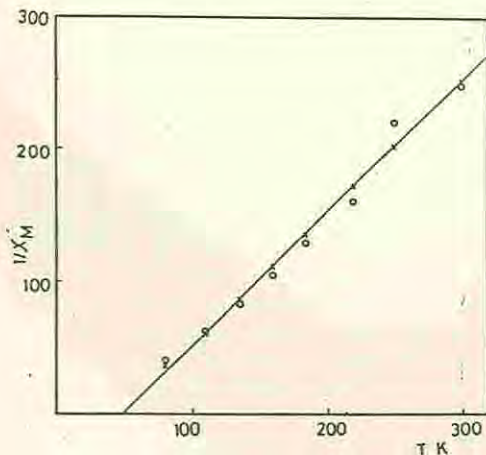
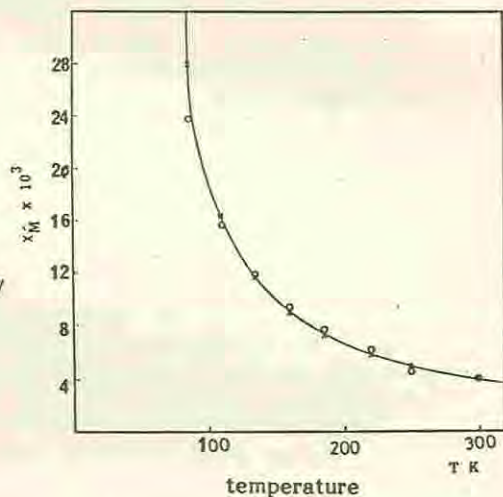


Fig. 2. The  $1/\chi_M$  vs temperature curve for  $\text{Ni}(4\text{-Etpy})_4(\text{N}_3)_2$ ; ( $\ast$ ) calculated  $1/\chi_M$  (according to Curie-Weiss equation),  $\circ$  experimental  $1/\chi_M$ .



For the three bis-(pyridine) complexes, the magnetic data obey the Curie-Weiss law in the 80-300 K range, but the  $\theta$  values are great enough with  $L = 4$ -Brpy and 4-Acpy to suggest strong magnetic interactions. In the case of the  $\text{Ni}(4\text{-Cypy})_2(\text{N}_3)_2$  complex, the small value of  $\theta$  (3.3 K) suggests a weak magnetic interaction.

The magnetic interactions in these bis-(pyridine) complexes were further investigated by least-square fitting of their  $\chi_M$  vs T curves to two theoretical expressions, assuming dimeric structures for these complexes. In the first expression,  $\chi_M$  for a Ni(II) dimer is given by equation (1).

$$\chi_M = \frac{Ng^2\beta^2}{3K(T-\theta)} \left\{ \frac{30 \exp(6J/KT) + 6 \exp(2J/KT)}{5 \exp(6J/KT) + 3 \exp(2J/KT) + 1} \right\} + N\alpha \quad (1)$$

In this expression  $N$ ,  $\beta$ ,  $K$  and  $T$  have their usual meaning (14). The last term  $N\alpha$  is the temperature independent paramagnetism (TIP).

In the second expression, equation (2), Ginsberg et. al. (13) have considered

$$\chi_M = \frac{2Ng^2\beta^2}{3K} \left\{ \frac{F_1}{T - 4Z'J'F_1} + \frac{2F'}{1 - 4Z'J'F'} \right\} + N\alpha \quad (2)$$

the effects of single ion zero field interactions on the magnetic susceptibility of nickel dimers. In the above expression  $F_1$  and  $F'$  are complicated functions of temperature, zero-field splitting  $D$  and the intradimer exchange integral  $J$ . The effective interdimer exchange is  $Z \cdot J$ . The complete expressions are given in references (13) and (15). The results of such calculations compared to the experimental data are given in Table 4, and Fig. 3.

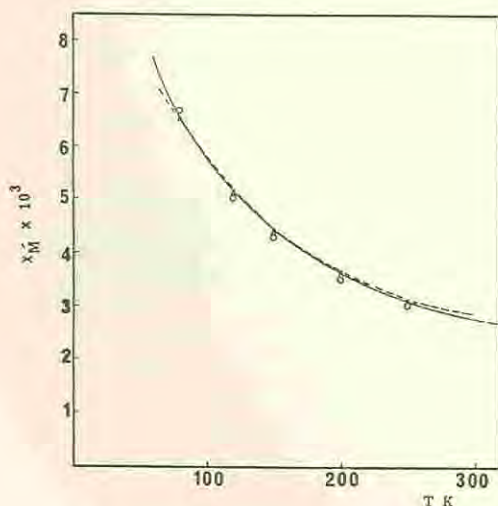


Fig. 3. The paramagnetic susceptibility data (cgsu/mole) vs temperature for  $\text{Ni}(4\text{-Acypy})_2(\text{N}_3)_2$ ; (\*—\*) calculated  $\chi_M$  values (according to equation 1), (----) calculated  $\chi_M$  values (according to equation 2), o experimental  $\chi_M$

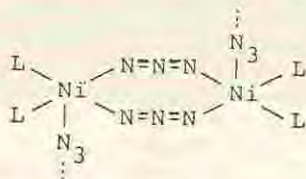


Fitting the  $\chi$  data (80-300 K) of  $\text{Ni}(4\text{-Acpy})_2(\text{N}_3)_2$  to equation (1) gave  $J = -0.26 \text{ cm}^{-1}$ ,  $g = 2.00$  and  $\theta = -72.9 \text{ K}$ , and to equation (2) gave  $J = -2.31 \text{ cm}^{-1}$ ,  $Z'J' = -26.36 \text{ K}$ ,  $g = 2.00$  and  $D = 0.002 \text{ cm}^{-1}$ . The parameters for the other compounds are given as footnotes under the respective tables. It is sufficient to note here that it has been shown (13,15) that fitting nickel(II) dimer data to the above equations gives accurate value of  $J$  as well as  $g$ . The parameters  $D$  and  $Z'J'$  are not well determined from magnetic susceptibility data (15) because the effects of those parameters are most important in the low-temperature region experimental uncertainties (temperature determination) and impurity effects are greatest.

It is clear that fitting the magnetic data for the three bis(pyridine) nickel(II) azide complexes to the above two equations leads to negative values of the singlet-triplet gap,  $J$ , thus indicating antiferromagnetic interactions. However, the small values of  $J$  for the 4-Acpy or 4-Cypy complexes may indicate weak antiferromagnetic exchange. For  $\text{Ni}(4\text{-Brpy})_2(\text{N}_3)_2$ ,  $J$  ranges from  $-34.3$  to  $-34.8 \text{ cm}^{-1}$  suggesting strong magnetic interactions.

As mentioned in the introduction, there are two di- $\mu$ -azido bridging modes for nickel(II) azide dimers; a single atom mode (A) or the end-to-end mode (B). If the bridging is of mode (A), the exchange coupling would be ferromagnetic in nature (6,7). However, if the bridging is end-to-end (mode B), then the exchange coupling would be expected to be antiferromagnetic and analogous to what is observed for other  $\mu(1,3)$ -azidonickel(II) dimers (16,17).

The electronic spectra of the three bis(pyridine) complexes are consistent with octahedral geometry around nickel(II) exhibiting the  ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ ,  $\nu_2$  transition, as a rather weak band around 640 nm (12). This structure implies bridges between  $\text{NiL}_2(\text{N}_3)_2$  molecules. As the pyridine ligands  $L$  are monodentate in these complexes, one of the two azide groups must bridge two metal atoms. The second azide either acts as a terminal group leading to five coordinate nickel(II) atoms or links other nickel(II) from an adjacent molecule at a long Ni-N distance forming a highly distorted octahedral structure. Alternatively, the first azide group links three different



nickel(II) atoms, as found in the complex  $\text{Cu}(\text{py})_2(\text{N}_3)_2$  (18), allowing the second azide to act as a monodentate ligand. However, in both cases the first azide group should be slightly asymmetric at least for the 4-Acpy and 4-Cypy complexes where  $J$  values are small. In any case the bridging azide group is not expected to be of mode (A). In both assumptions the infrared spectra are expected to show  $\nu_s(\text{N}_3)$  bands which are infrared-active for asymmetric azido ligands (1). This assumption may explain the appearance of the  $\nu_s(\text{N}_3)$  bands in the region  $1350\text{-}1280 \text{ cm}^{-1}$  in spectra of the three complexes (12). The results of the magnetic susceptibility measurements led us to assume that the three nickel(II) complexes are dimers having the mode (B) structure. Polymerization of the dimers may be attained through a long Ni-N bond with the end nitrogen of a terminal group. According to the obtained values of  $J$ , the degree of asymmetry of  $\mu(1,3)$  azide group (i.e. the difference between the two N-N lengths) increases in the order  $4\text{-Acpy} > 4\text{-Cypy} \gg 4\text{-Brpy}$ . In this dimer structure one assumes that the highest occupied molecular orbital  $\pi_g$  of the azide group plays an important role (5-7).



In this orbital at a given instant, an electron with, say,  $\alpha$  spin is localized around one of the terminal nitrogen atoms, and the other electron with the  $\beta$  spin is localized around the other nitrogen atom. The interaction between these  $\pi_g$  and the magnetic orbitals on nickel(II) ions in the above fashion gives rise to a MO in which the electron with  $\alpha$ -spin is delocalized toward one of the nickel(II) ions (e.g. **A**) and the other electron with the  $\beta$  spin is delocalized toward the other nickel(II) ion (**B**). Thus the unpaired electrons around **A** will have a probability of spin  $\alpha$  larger than 1/2 and the unpaired electron around **B** with a probability of a spin  $\alpha$  larger than 1/2, which favours the antiferromagnetic interaction.

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