Binuclear Nickel(II) and Cobalt(III) Complexes with Dissimilar Bridges: Synthesis, Spectroscopy, Crystal Structure, and Magnetism

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Two novel binuclear nickel(II) and cobalt(III) complexes with two or three dissimilar bridges, $[Ni_2(tacn)_2(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh)](ClO_4) \cdot H_2O$ (**1**) and $[Co_2(tacn)_2(\mu\text{-}N_3)(\mu\text{-}OH)(\mu\text{-}O_2CPh)](ClO_4)_3$ (**2**) (tacn = 1,4,7-triazacyclononane), were synthesized and structurally as well as magnetically characterized. Both compounds have a discrete binuclear structure, bridged by two N_3^- ions and one carboxylato group of the benzoate ion for **1** and one N_3^- ion, one carboxylato group of the benzoate ion, and one hydroxy group for **2**; the macrocyclic ligand tacn acts as terminal ligand. The magnetic data of compound **1** were analyzed by means of $\hat{H} = -2J\hat{S_1}\hat{S_2} - D(\hat{S_1^2} + \hat{S_2^2})$, leading to $J = 19.6$ cm^{-1}, $g = 2.07$, $D = 4.01$ cm^{-1}, and $zJ' = -0.32$ cm^{-1}. The ferromagnetic interaction is discussed on the basis of the structural features.

Introduction. – Molecular magnetism of polynuclear complexes is of considerable interest both for designing new magnetic materials with potential use in information storage and for investigating the relationship between the sturcture and the role of the polymetallic active sites in biological systems [1–4]. Particular emphasis has been placed in the magnetisms of μ-azidonickel(II) complexes [5–25]. From a magnetic point of view, the most interesting characteristic of these azidonickel systems lies in the fact that the azido ligand represents a very effective superexchange pathway in its two coordination modes, end-to-end, which always gives antiferromagnetic behavior, and end-on, which always gives ferromagnetic coupling.

As for end-on azidonickel(II) complexes, *Ribas* and co-workers proposed that the parameter J could be correlated only with the Ni−N−Ni value in the sense that greater Ni−N−Ni angles correspond to a most effective ferromagnetic superexchange [10]. This result was confirmed by *Ruiz et al.*, who recently reported the density functional calculations on magnetic coupling in end-on azidonickel(II) complexes, indicating that J increases upon increasing the Ni−N−Ni angle from 80° to 104°, while J deceases as the bond distance of Ni−(μ-N) increases [26]. Moreover, *Christou* and co-workers believe that there is non-dependence of J on the Ni−N−Ni angle or the Ni−Ni−N−N torsion angle for these compounds; however, there appears to be a trend for J to become more ferromagnetic with increasing average Ni−(μ-N) distances [17].

On the other hand, considerable attention has been devoted to dinuclear Cu^{II} complexes with two dissimilar bridges [27–34]. Orbital complementary and counter-complementary effects have been proposed by *Nishida* and co-workers [28] and *Reed* and co-workers [29] to explain the unusual magnetic properties in the mixed-bridged

Cu^{II} complexes. However, little work has been attended to the design of other mixed-bridged metal complexes, except Cu^{II} compounds [8][35–38].

With these facts in mind, our synthetic strategy was to construct ferromagnetically coupled binuclear compounds with dissimilar bridges other than Cu^{II} complexes. To build the desired molecular architecture, we chose Ni^{II} and Co^{II} as metal building blocks, azido and benzoato as bridging ligands, and the macrocyclic ligand 1,4,7-triazacyclononane (tacn) as terminal ligand due to its rigidity, and succeeded in obtaining crystalline samples of two binuclear complexes with dissimilar bridges, i.e., $(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh)[Ni_2(tacn)_2](ClO_4)\cdot H_2O$ (**1**) and $[Co_2(\mu\text{-}N_3)(\mu\text{-}OH)\mu\text{-}O_2CPh)(tacn)_2]$-$(ClO_4)_3$ (**2**). The crystal structures and magnetic properties of **1** and **2** were investigated.

Results and Discussion. – *Synthetic Aspects*. In a sense, our synthetic strategy succeeded through a rational assembly: macrocyclic ligand tacn acts as a terminal ligand, and a benzoato bridge forces two Ni^{II} or Co^{III} centers so close together that the azido ligand has to bind two metals in an end-on fashion. Comparison can be made to compounds synthesized by *Wieghardt* and co-workers in a similar way, but in the absence of sodium benzoate with the macrocyclic ligands 1,5,9-triazacyclododecane and 1,4,7-trimethyl-1,4,7-triazacyclononane, which show two and three end-to-end N_3^- bridges, respectively [5].

As for complex **2**, we believe that the macrocyclic Co^{II} compound probably was oxidized to Co^{III} before and/or when sodium azide was added. The reaction might be $2[Co_2(\mu\text{-}O_2CPh)(tacn)_2]^{3+} + 2H_2O + O_2 \rightarrow 2[Co_2(\mu\text{-}OH)(\mu\text{-}O_2CPh)(tacn)_2]^{4+} + 2OH^-$. Thus, the final compound is the binuclear compound with three dissimilar bridges: $[Co_2(\mu\text{-}N_3)(\mu\text{-}OH)(\mu\text{-}O_2CPh)(tacn)_2] (ClO_4)_3$ (**2**).

*Molecular Structure of $[Ni_2(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh)(tacn)_2](ClO_4)\cdot H_2O$ (**1**)*. The structure of complex **1** consists of binuclear $[Ni_2(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh)(tacn)_2]^+$ cations, perchlorate anions, and H_2O molecules. A perspective view of the binuclear cation with two dissimilar bridges is shown in *Fig. 1*, and selected bond lengths and angles are listed in *Table 1*.

In the binuclear cation, two Ni^{II} atoms are bridged by two N_3^- ions and the carboxylato group of the benzoate ion; the macrocyclic ligand tacn acts as terminal ligand. Each Ni^{II} atom is six-coordinated, forming a slightly distorted octahedral geometry. The Ni−N bond distance is in the range of 2.079(4)–2.131(4) Å, which is normal for Ni−N coordination bonds. The Ni−O bond distance is averaged to 2.074 Å, which is also very close to that of the literature [17][35]. The Ni···Ni distance in the binuclear cation is averaged to 3.112 Å.

Fig. 2 shows the packing diagram of complex **1**. Perchlorate anions and H_2O molecules lie in the space between binuclear $[Ni_2(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh](tacn)]^+$ cations. H-Bonds are firstly found between the carboxylato O-atom (O(1A)) and non-coordinated H_2O (O(7A)) molecules with a distance of 2.918 Å. The second kind of H-bonds exists between the C-atoms of tacn and O-atoms of the perchlorate anions (C(7A)−O(6A) 3.478 Å, C(9B)−O(5A) 3.309 Å), which link adjacent binuclear $[Ni_2(\mu\text{-}N_3)_2(\mu\text{-}O_2CPh)(tacn)]^+$ together to form a unique one-dimensional structure. *Desiraju* believes that because of the weakness of the interaction, C−H···O bonds can be distorted by other crystal forces and that C···O distances (D) of 3.0–4.0 Å are
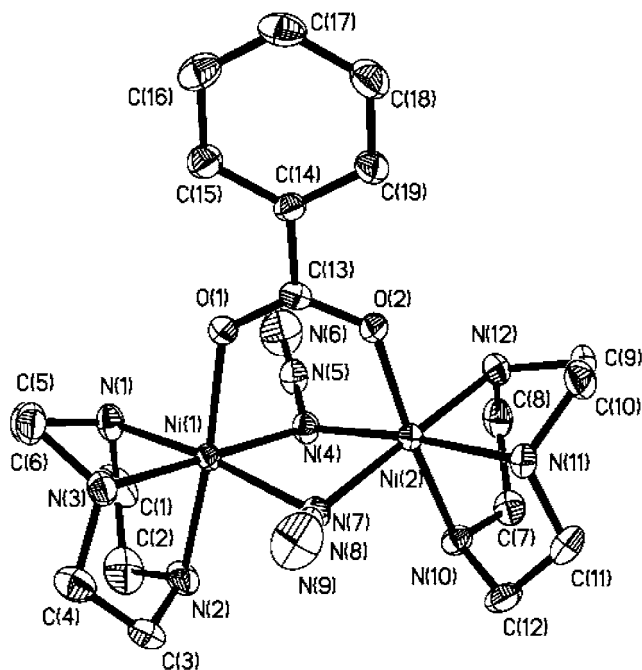
Fig. 1. *Perspective view of the [Ni$_2$(μ-N$_3$)$_2$(μ-O$_2$CPh)(tacn)$_2$]$^+$ cation of **1** with the labeling scheme*

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for **1***

Ni(1)−N(2)	2.082(4)	Ni(2)−O(2)	2.039(3)
Ni(1)−N(4)	2.091(4)	Ni(2)−N(10)	2.079(4)
Ni(1)−N(1)	2.093(4)	Ni(2)−N(12)	2.090(4)
Ni(1)−N(3)	2.096(4)	Ni(2)−N(11)	2.101(4)
Ni(1)−O(1)	2.109(3)	Ni(2)−N(7)	2.131(4)
Ni(1)−N(7)	2.131(4)	Ni(2)−N(4)	2.131(4)
N(2)−Ni(1)−N(4)	96.94(17)	O(2)−Ni(2)−N(10)	174.66(14)
N(2)−Ni(1)−N(1)	82.94(18)	O(2)−Ni(2)−N(12)	93.48(15)
N(4)−Ni(1)−N(1)	96.57(17)	N(10)−Ni(2)−N(12)	83.91(16)
N(2)−Ni(1)−N(3)	83.63(16)	O(2)−Ni(2)−N(11)	91.38(15)
N(4)−Ni(1)−N(3)	179.37(16)	N(10)−Ni(2)−N(11)	83.72(16)
N(1)−Ni(1)−N(3)	83.77(17)	N(12)−Ni(2)−N(11)	83.83(16)
N(2)−Ni(1)−O(1)	173.89(15)	O(2)−Ni(2)−N(7)	87.50(14)
N(4)−Ni(1)−O(1)	89.06(15)	N(10)−Ni(2)−N(7)	95.14(15)
N(1)−Ni(1)−O(1)	95.25(15)	N(12)−Ni(2)−N(7)	178.96(16)
N(3)−Ni(1)−O(1)	90.38(14)	N(11)−Ni(2)−N(7)	96.49(16)
N(2)−Ni(1)−N(7)	89.18(17)	O(2)−Ni(2)−N(4)	94.00(14)
N(4)−Ni(1)−N(7)	82.61(15)	N(10)−Ni(2)−N(4)	90.98(16)
N(1)−Ni(1)−N(7)	171.93(16)	N(12)−Ni(2)−N(4)	97.91(16)
N(3)−Ni(1)−N(7)	97.12(16)	N(11)−Ni(2)−N(4)	174.23(16)
O(1)−Ni(1)−N(7)	92.76(14)	N(7)−Ni(2)−N(4)	81.68(15)
C(13)−O(1)−Ni(1)	126.3(3)	Ni(1)−N(4)−Ni(2)	94.98(17)
C(13)−O(2)−Ni(2)	130.4(3)	Ni(1)−N(7)−Ni(2)	93.79(16)

common [39]. For the Ni^{II} complex **1**, the average $C \cdots O$ distance is 3.393 Å, which is much longer than that of $O(7A) \cdots O(1A)$ (2.918 Å). Another interesting feature is that the benzene rings of the benzoato ligands of different cations are parallel, as seen in *Fig. 2*. However, we believe that prolably no π-π interaction exists because the distance between the C-atoms of the benzene rings is too large (6.155 – 6.426 Å).
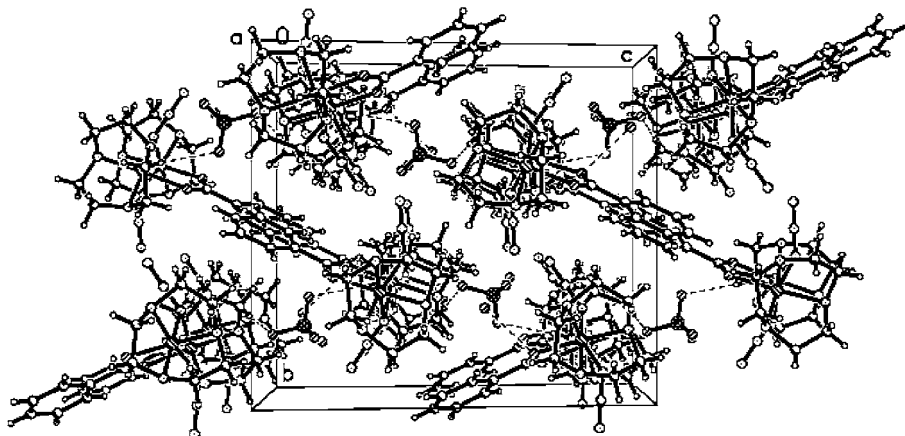

Fig. 2. *Packing diagram of complex* **1**

Molecular Structure of [Co$_2$(μ-N$_3$)(μ-OH)(μ-O$_2$CPh)(tacn)$_2$](ClO$_4$)$_3$ (**2**). The structure of complex **2** consists of binuclear [Co$_2$(μ-N$_3$)(μ-OH)(μ-O$_2$CPh)(tacn)$_2$]$^{3+}$ cations and perchlorate anions. A perspective view of the binuclear cation with three dissimilar bridges is depicted in *Fig. 3*, and selected bond lengths and angles are listed in *Table 2*.

In the binuclear cation, two Co^{III} atoms are bridged by one N$_3^-$ ion, one carboxylato group of the benzoate ion, and one hydroxy group; the macrocyclic ligand tacn acts as terminal ligand. Each Co^{III} atom is six-coordinated, forming a distorted octahedron. The averaged $Co-N$ and $Co-N$ bond distances are 1.937 and 1.914 Å, respectively, all being normal coordination bonds. The $Co \cdots Co$ distance in the binuclear cation is averaged to 2.868 Å.

Fig. 4 shows the packing diagram of complex **2**. Perchlorate anions lie in the space between the binuclear [Co$_2$(μ-N$_3$)(μ-OH)(μ-O$_2$CPh)(tacn)$_2$]$^{3+}$ cations. H-Bonds are found between O-atoms from perchlorate anions and N-atoms or C-atoms of the terminal tacn ligand ($O(14A) \cdots N(1BA)$ 2.933 Å, $O(22A) \cdots C(5BA)$ 3.122 Å).

Spectroscopic Properties. The IR spectra of the two complexes **1** and **2** are very similar, both displaying the presence of the benzoato ligand with $\tilde{\nu}_{asym}(O-C-O)$ at 1590v*s* and 1600v*s* cm^{-1} as well as the $\tilde{\nu}_{asym}(N_3^-)$ bands centered at 2000v*s* and 2005v*s* cm^{-1} for **1** and **2**, respectively (v*s* = very strong). The absorptions at 3250*s* and 3150*s* are assigned to $\tilde{\nu}(N-H)$ of the macrocyclic ligand tacn and to H$_2$O for complex **1** or OH$^-$ for **2** (*s* = strong). The absorption at 1100v*s* cm^{-1} is the characteristic band of ClO$_4^-$. The other two bands of the N$_3^-$ ligand ($\tilde{\nu}_{sym}$ and δ) are masked by bands of the tacn ligand and the $\tilde{\nu}_{sym}(O-C-O)$ bands and perchlorate bands.

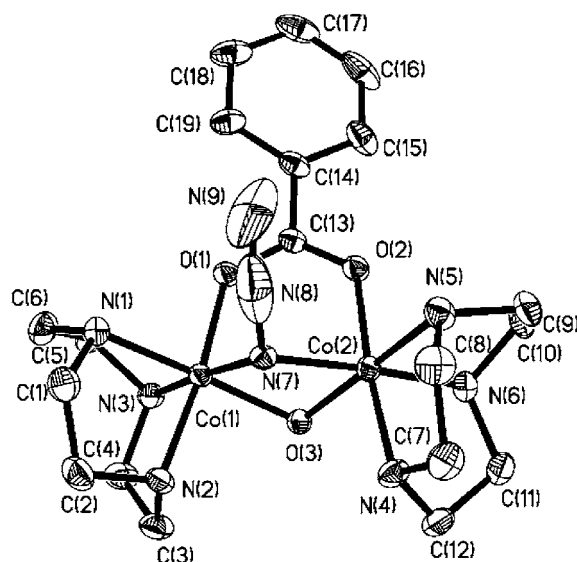Fig. 3. *Perspective view of [Co$_2$(μ-N$_3$)(μ-OH)(μ-O$_2$CPh)(tacn)$_2$]$^{3+}$ cation of* **2** *with the labeling scheme*

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **2**

Co(1)–O(1)	1.902(3)	Co(2)–O(3)	1.907(3)
Co(1)–N(7)	1.915(4)	Co(2)–O(2)	1.922(3)
Co(1)–O(3)	1.924(3)	Co(2)–N(7)	1.935(4)
Co(1)–N(2)	1.939(4)	Co(2)–N(5)	1.939(4)
Co(1)–N(1)	1.940(4)	Co(2)–N(4)	1.942(4)
Co(1)–N(3)	1.943(4)	Co(2)–N(6)	1.949(4)
Co(1)–Co(2)	2.8681(9)		
O(1)–Co(1)–N(7)	91.13(16)	O(3)–Co(2)–O(2)	93.56(14)
O(1)–Co(1)–O(3)	94.79(14)	O(3)–Co(2)–N(7)	79.64(15)
N(7)–Co(1)–O(3)	79.73(15)	O(2)–Co(2)–N(7)	92.79(16)
O(1)–Co(1)–N(2)	173.63(16)	O(3)–Co(2)–N(5)	175.83(17)
N(7)–Co(1)–N(2)	93.22(17)	O(2)–Co(2)–N(5)	88.96(17)
O(3)–Co(1)–N(2)	90.58(16)	N(7)–Co(2)–N(5)	96.92(18)
O(1)–Co(1)–N(1)	88.07(16)	O(3)–Co(2)–N(4)	90.87(16)
N(7)–Co(1)–N(1)	98.14(18)	O(2)–Co(2)–N(4)	174.45(17)
O(3)–Co(1)–N(1)	176.45(16)	N(7)–Co(2)–N(4)	91.30(18)
N(2)–Co(1)–N(1)	86.70(18)	N(5)–Co(2)–N(4)	86.83(19)
O(1)–Co(1)–N(3)	88.79(16)	O(3)–Co(2)–N(6)	96.15(17)
N(7)–Co(1)–N(3)	174.60(18)	O(2)–Co(2)–N(6)	89.11(17)
O(3)–Co(1)–N(3)	94.89(16)	N(7)–Co(2)–N(6)	175.48(18)
N(2)–Co(1)–N(3)	87.33(17)	N(5)–Co(2)–N(6)	87.2(2)
N(1)–Co(1)–N(3)	87.26(18)	N(4)–Co(2)–N(6)	87.1(2)
C(13)–O(1)–Co(1)	127.6(3)	Co(2)–O(3)–Co(1)	96.95(15)
C(13)–O(2)–Co(2)	126.2(3)	Co(1)–N(7)–Co(2)	96.31(17)

The UV and VIS spectra were measured in the 200–1000 nm range. The spectra of complex **1** show a strong absorption band at 34500 cm^{-1} ($\varepsilon > 10^3$ l·mol^{-1}·cm^{-1}), which may be attributed to a charge transfer and the transition of the ligand itself. In addition,
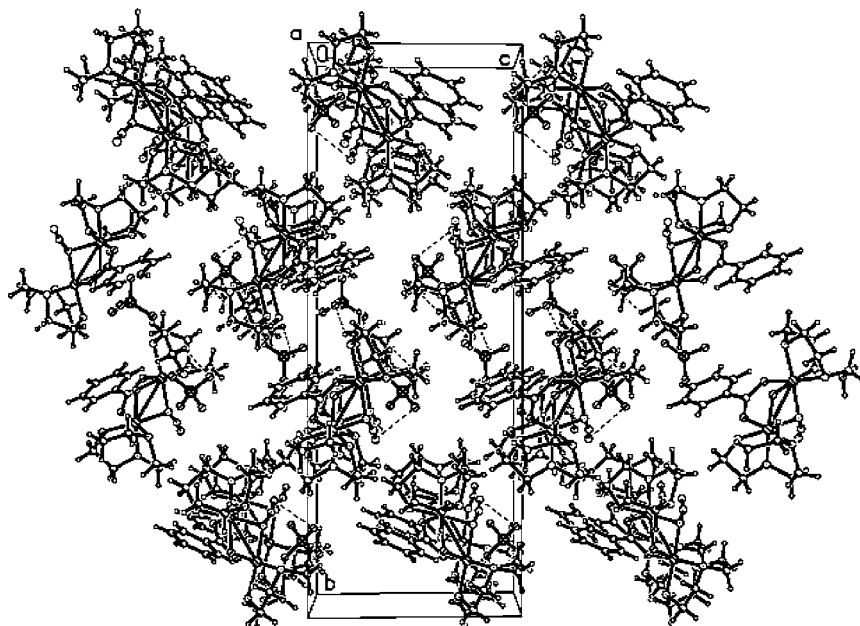
Fig. 4. *Packing diagram of complex* **2**

three bands of medium intensity at 11200 ($\tilde{\nu}_1$; $\varepsilon = 27.1$ l·mol^{-1}·cm^{-1}), 17300 ($\tilde{\nu}_2$; $\varepsilon = 9.56$ l·mol^{-1}·cm^{-1}), and 28000 cm^{-1} ($\tilde{\nu}_3$; $\varepsilon = 15.1$ l·mol^{-1}·cm^{-1}) are tentatively attributed to the transitions of the Ni^{II} ions in a symmetry close to an octahedral environment: $\tilde{\nu}_1$, $^3A_{2g} \rightarrow {}^3T_{2g}$; $\tilde{\nu}_2$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F); $\tilde{\nu}_3$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P); these are in agreement with those given in the literature for similar octahedral Ni^{II} compounds [16][17][23][35][40]. According to the ligand-field theory [41], 10Dq, B, and $\tilde{\nu}_2$ can be obtained by using two observed bands ($\tilde{\nu}_1$ and $\tilde{\nu}_3$): 10$Dq = 11200$ cm^{-1}, $B = 806.85$ cm^{-1}, and $\tilde{\nu}_2$ (calc.) = 17574 cm^{-1}. The calculated value of $\tilde{\nu}_2$ is close to the observed one, indicating that the assignments are reasonable. The calculated nephelauxetic parameters $\beta = B_{complex}/B_{free} = 0.764$ (considering $B = 1056$ cm^{-1} for the gaseous ion (^3P) Ni^{2+}) shows moderately strong covalent bonding of Ni^{II} in this complex.

For complex **2**, the spectra also show a strong absorption band at 29000 cm^{-1} ($\varepsilon > 10^3$ l·mol^{-1}·cm^{-1}) and one band of medium intensity at 19100 cm^{-1} ($\tilde{\nu}_2$, $\varepsilon = 10^2$ l·mol^{-1}·cm^{-1}). From comparison with similar compounds, this latter absorption may be attributed to the d-d transitions of low-spin Co^{III} ions in an octahedral environment, *i.e.*, to $\tilde{\nu}_2$ ($^1A_{1g} \rightarrow {}^1T_{1g}$) according to the strong-field approximation. However, the former may be attributed to a charge transfer and the transition of the ligand itself, together with the $\tilde{\nu}_1$ ($^1A_{1g} \rightarrow {}^1T_{2g}$) transition [42].

Magnetic Properties. The magnetic susceptibility was measured in the temperature range 4–300 K with an applied magnetic field of 1 T. As shown in *Fig. 5*, for complex **1**, the room-temperature value for the effective magnetic moment μ_{eff} (4.32 B.M.) is a little higher than that expected for two isolated Ni^{II} ions ($\mu_{eff} = 4.0$ B.M.). Upon cooling, the μ_{eff} value steadily increases to reach a maximum value of 5.19 B.M. at *ca.*

18 K, suggesting that a ferromagnetic interaction between Ni^{II} ions is operative. This maximum value may be compared to the spin-only value ($\mu_{eff} = 4.90$ B.M.) calculated for an $S = 4/2$ ground-state expected for two ferromagnetically coupled high-spin Ni^{II} ions with $g = 2.00$; the actual g value for Ni^{II} is expected to be a little higher than 2.00, however. Below 18 K, the μ_{eff} value slightly decreased on further cooling, which may be the result of intermolecular interactions.
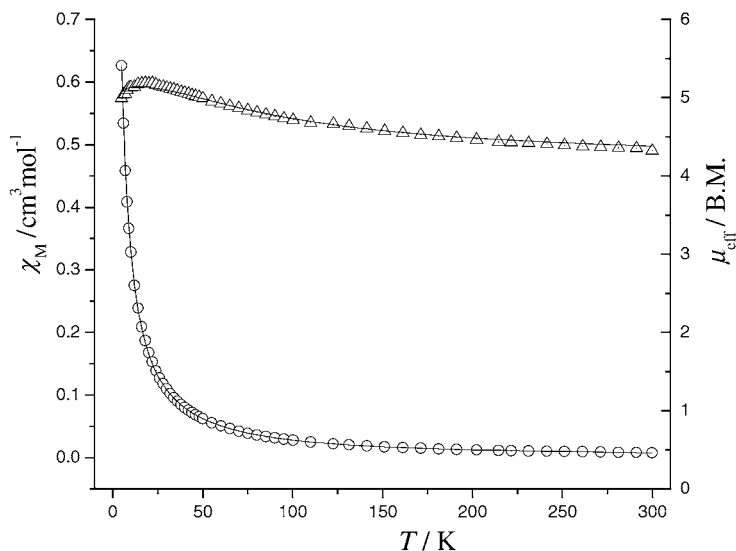

Fig. 5. *Experimental and calculated variations of χ_M (O) and μ_{eff} ($\triangle$) vs. T for complex* **1**

The magnetic analysis was carried out by using the spin Hamiltonian $\hat{H} = -2J\hat{S_1}\hat{S_2} - D(\hat{S_1}^2 + \hat{S_2}^2)$ and involved the intermolecular exchange interaction (zJ') in the molecular-field approximation; the resulting magnetic susceptibility is given by *Eqn. 1*.

$$\chi_M = \frac{2N\beta^2 g^2}{KT}\left[\frac{4\exp(A) + \exp(B) + \exp(G)}{2\exp(A) + 2\exp(B) + \exp(C) + 2\exp(G) + \exp(E) + \exp(F)}\right] + N_\alpha \quad (1)$$

$$\chi_M' = \frac{\chi_M}{1 - (2zJ'/Ng^2\beta^2)\chi_M}$$

$$A = (6J + 2D)/KT$$

$$B = (6J + D)/KT$$

$$C = [(3J + D) - (9J^2 - 2DJ + D^2)^{1/2}]/KT$$

$$G = (2J + D)/KT$$

$$E = (2J + 2D)/KT$$

$$F = [(3J + D) + (9J^2 - 2DJ + D^2)^{1/2}]/KT$$

Therein, J is the intramolecular exchange integral, D the zero-field splitting parameter, and N_α the temperature-independent paramagnetism ($200 \cdot 10^{-6}$ cm^3 mol^{-1}), and the other symbols have their usual meanings. The best fitting for the experimental data gives $J = 19.6$ cm^{-1}, $g = 2.07$, $D = 4.01$ cm^{-1}, and $zJ' = -0.32$ cm^{-1}. The agreement factor $R = \Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi^2_{obs.}$ is $8.3 \cdot 10^{-5}$.

On comparison with the known structural data of similar octahedral Ni^{II} complexes containing μ-(azido-$\kappa N,\kappa N$) bridges (see *Table 3*), we found that both Ni$\cdots$Ni and Ni$-$N$-$Ni$_{av}$ of complex **1** are largely different from the corresponding literature values. There seems to be no obvious correlation between J and the Ni$-$N$-$Ni$_{av}$ angle or Ni$\cdots$Ni distance in these azidonickel(II) species. Moreover, when we use the assumption of *Christou* and co-workers [17], still no simple linear correlation between J and Ni$-$(μ-N)$_{av}$ is revealed. Since a 'syn-syn' carboxylato bridge provides a small metal-metal distance and results in a good overlap of the magnetic orbitals, an antiferromagnetic coupling is always induced [43]. Therefore, it is difficult to correlate the J value with the structural data of complex **1** because only the average value due to the influence of both the μ-(azido-$\kappa N,\kappa N$) (ferromagnetic) and carboxylato (antiferromagnetic) bridges was obtained. The observed J value of complex **1** is close to that of other azidonickel(II) species, which can only indicate that the azido ligand is the dominant factor in the superexchange interaction, and a moderately ferromagnetic interaction is operative even in such Ni^{II} complexes with dissimilar bridges. A similar ferromagnetic interaction has been found in a tetranuclear Ni^{II} complex with the dissimilar OH$^-$ and N$_3^-$ bridges and 1,3-diaminopropan-2-ol (OHpn) as blocking ligand [8]. *Kahn* and co-workers explain the observed ferromagnetism by polarization effects [44][45], and hence, spin polarization may well be the key feature leading to ferromagnetism in this azidonickel(II) complexes.

Table 3. *Structural and Magnetochemical Data for Known Octahedral Nickel(II) Complexes Containing the μ-(Azido-κN,κN) Bridge and of Complex* **1**[a])

	Ni$-$(μ-N)$_{av}$ [Å]	Ni$\cdots$Ni [Å]	Ni$-$N$-$Ni$_{av}$ [deg]	J [cm^{-1}]	Ref.
[Ni$_2$(μ-N$_3$)$_2$(en)$_4$] (ClO$_4$)$_2$	2.134	3.369	104.3	20.9	[13]
[Ni$_2$(μ-N$_3$)$_4$(en)$_2$]$_n$	2.121	3.241	100.6	14.8	[13]
[Ni$_2$(μ-N$_3$)$_4$(tn)$_2$]$_n$	2.106	3.310	103.7	17.6	[13]
[Ni$_2$(μ-N$_3$)$_2$(N$_3$)$_2$(terpy)$_2$]$\cdot$2H$_2$O	2.118	3.276	101.3	20.1	[6]
[Ni$_2$(μ-N$_3$)$_2$(Me$_3$[12]N$_3$)$_2$] (ClO$_4$)$_2$$\cdot$2H$_2$O	2.080	3.273	103.8	43.9	[10]
[Ni$_2$(μ-N$_3$)$_2$(232-tet)$_2$] (ClO$_4$)$_2$	2.167	3.423	104.9	33.8	[10]
[Ni$_2$(μ-N$_3$)$_2$(232-tet)$_2$] (PF$_6$)$_2$	2.180	3.449	104.6	17.2	[20]
[Ni$_2$(μ-N$_3$)$_2$(N$_3$)$_2$(pepci)$_2$]	2.127	3.297	101.6	36.3	[7]
[Ni$_2$(μ-N$_3$)$_2$(N$_3$)$_2$(Medpt)$_2$][b])	2.193	3.448	103.7	46.7	[16]
	2.202	3.470	104.0		
[Ni$_4$(μ-N$_3$)$_4$(Opn)$_2$(OHpn)$_2$] (ClO$_4$)$_2$	2.122	3.206	98.1	21.3	[8]
[Ni$_2$(μ-N$_3$)$_2$(μ-O$_2$CPh)(tacn)$_2$] (ClO$_4$)$\cdot$H$_2$O (**1**)	2.121	3.112	94.4	19.6	this work

[a]) en = Ethane-1,2-diamine, tn = N,N-bis(2-aminoethyl)ethane-1,2-diamine, terpy = 2,2′:6′,2′′-terpyridine, Me$_3$[12]N$_3$ = 1,5,9-trimethyl-1,5,9-triazacyclododecane, 232-tet = N,N′-bis(2-aminoethyl)-1,3-propanediamine, pepci = N′-(2-pyridin-2-ylethyl)pyridine-2-carbalimide, Medpt = methyl-bis(3-aminopropyl)amine, OHpn = 1,3-diaminopropan-2-ol, tacn = 1,4,7-triazacyclononane. [b]) Complex shows a magnetic transition at 150 – 120 K. Parameters given are for the low- and high-temperature forms, respectively.

The magnetic properties of complex **2** were determined at both room and liquid-nitrogen temperatures. The results indicated that this complex is diamagnetic, which is in agreement with the strong-field approximation for Co^{III} in the UV/VIS-spectrum analysis.

Conclusion. – Two novel binuclear Ni^{II} and Co^{III} complexes with dissimilar bridges were synthesized and structurally as well as magnetically characterized. Both compounds have a discrete binuclear structure, bridged by two N_3^- ions and one carboxylato group of the benzoate ion for **1**, and by one N_3^- ion, one carboxylato group of the benzoate ion, and one OH ligand for **2**. The magnetic data of **1** was analyzed by means of $\hat{H} = -2J\hat{S_1}\hat{S_2} - D(\hat{S_1}^2 + \hat{S_2}^2)$, leading to $J = 19.6$ cm^{-1}, $g = 2.07$, $D = 4.01$ cm^{-1}, and $zJ' = -0.32$ cm^{-1}. The observation of a ferromagnetic interaction within complex **1** indicates that in this mixed-bridged complex, the N_3^- bridge is the dominant factor in the superexchange interaction, and a moderately ferromagnetic interaction is operative even in the Ni^{II} complexes with dissimilar bridges.

Experimental Part

General. The ligand 1,4,7-triazacyclononane was prepared as previously described [46][47]. All other starting materials were purchased from the *Tianjin Chemical Company* and were of reagent grade. UV/VIS Spectra: *Shimadzu UV-2101-PC* spectrophotometer; in H$_2$O. IR Spectra: KBr discs; *Shimadzu IR-408* spectrophotometer; in 4000–600 cm^{-1} region. Variable-temperature magnetic susceptibilities: *Quantum-Design MPMS-7 SQUID* magnetometer, applied magnetic field, 1 T; diamagnetic corrections were made with *Pascal*'s constants for all the constituent atoms [48]. Elemental analyses: *Perkin-Elmer* analyzer, model *240*.

Bis[μ-(azido-κN:κN)][μ-(benzoato-κO:κO')]bis(1,4,7-triazacyclononane-κN',κN⁴,κN⁷)dinickel(1+) Perchlorate Hydrate (**1**). A MeOH soln. (10 ml) of sodium benzoate (108 mg, 0.75 mmol) was added to an aq. soln. of (10 ml) of Ni(ClO$_4$)$_2 \cdot$ 6 H$_2$O (549 mg, 1.5 mmol). Then 1,4,7-triazacyclononane (193.5 mg, 1.5 mmol) and NaN$_3$ (97.5 mg, 1.5 mmol) were added in turn. After 1/2 h heating at 50–70°, the mixture was filtered. The filtrate was left undisturbed, and well-formed blue crystals of **1** were obtained by evaporation at r.t. after a week. Anal. calc. for C$_{19}$H$_{37}$ClNi$_2$N$_{12}$O$_7$: C 32.67, H 5.30, N 24.07; found: C 32.79, H 5.00, N 23.95.

[μ-(Azido-κN:κN)][μ-(benzoato-κO:κO')](μ-hydroxy)bis(1,4,7-triazacyclononane-κN¹,κN⁴,κN⁷)dicobalt(3+) Triperchlorate (**2**). Complex **2** was prepared as described for **1**, with Co(ClO$_4$)$_2 \cdot$ 6 H$_2$O (549 mg, 1.5 mmol) instead of Ni(ClO$_4$)$_2 \cdot$ 6 H$_2$O. Light red crystals. Anal. calc. for C$_{19}$H$_{36}$Cl$_3$Co$_2$N$_9$O$_{15}$: C 26.69, H 4.21, N 14.75; found: C 26.60, H 4.47, N 14.97.

X-Ray Crystallography. Crystals of dimensions 0.25 mm × 0.20 mm × 0.20 mm for **1** and 0.88 mm × 0.24 mm × 0.22 mm for **2** were mounted on a *Bruker Smart-1000* area detector and a *Siemens Smart CCD*, resp., and graphite-monochromated MoK_a radiation ($\lambda = 0.71073$ Å) at 293(2) K was applied. The structures were solved by direct methods and successive *Fourier* difference syntheses (SHELXS-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-H-atoms (SHELXL-97) [49]. Crystal data and details of the structure determination are summarized in *Table 4*. Crystallographic data (excluding structure factors) for the structure analysis have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication Nos. 200606 for **1** and 200605 for **2**, resp. Copies of the data can be obtained, free of charge, from the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 4. *Crystal Data and Details of the Structure Determination of Complexes* **1** *and* **2**

	1	**2**
Empirical formula	$C_{19}H_{37}ClN_{12}Ni_2O_7$	$C_{19}H_{36}Cl_3Co_2N_9O_{15}$
M_r	698.48	854.3
Crystal system	monoclinic	monoclinic
Space group	$P2(1)/c$	$P2(1)/n$
a [Å]	12.347(4)	9.7391(3)
b [Å]	14.759(5)	29.5574(9)
c [Å]	16.624(5)	11.0734(3)
β [°]	99.200(5)	94.1190(10)
V [Å³]	2990.5(15)	3179.38(16)
Z	4	4
$\mu(MoK_a)$ [mm^{-1}]	1.407	1.414
$F(000)$	1456	2324
θ Range [°]	2.17 to 25.03	1.38 to 25.05
Limiting indices	$-14 \leq h \leq 9, -16 \leq k \leq 17,$ $-19 \leq l \leq 19$	$-11 \leq h \leq 11, -35 \leq k \leq 22,$ $-12 \leq l \leq 13$
Total reflections	12109	11067
Unique reflections	5231	5589
R(int)	0.0563	0.0273
Data, restraints, parameters	5231, 0, 370	5589, 0, 433
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0650P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 8.4975P]$, $P = (F_o^2 + 2F_c^2)/3$
Final R indices ($I > 2\,\sigma(I)$)	0.0473, 0.1081	0.0582, 0.1460
R indices (all data)	0.0900, 0.1263	0.0754, 0.1572
Goodness-of-fit on F^2	0.943	1.059
Largest diff. peak and hole [eÅ^{-3}]	0.826, -0.620	0.919, -0.846

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