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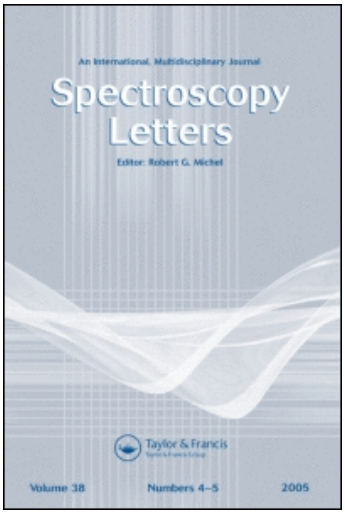

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Synthesis, Magnetic and Spectral Properties of One-dimension Chain Adducts of $Ni(Bu\text{-}dtp)_2$, NiQ_2 and $Ni(TTA)_2$ with 4,4'-bipyridine. Crystal Structure of $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$ (Bu-dtp=dibutyldithiophosphate, Q=8-quinolinol, TTA=4,4,4-trifluoro-l-(2-thienyl)-l,3-butanedionate,4,4'-bipy=4,4'-bipyridine)

Ren-Gen Xiong[a]; Zhi Yu[a]; Jing-Lin Zuo[a]; Xiao-Zeng You[a]; Xiao-Ying Huang[b]
[a] Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P. R. China [b] State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, P. R. China

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Synthesis, Magnetic and Spectral Properties of One-dimension Chain Adducts of $Ni(Bu\text{-}dtp)_2$, NiQ_2 and $Ni(TTA)_2$ with 4,4'-bipyridine. Crystal Structure of $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$ (Bu-dtp=dibutyldithiophosphate, Q=8-quinolinol, TTA=4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate ,4,4'-bipy=4,4'-bipyridine)

Key words: Synthesis; Magnetism; Spectral properties; One-dimension; Chain and Adduct.

Ren-Gen Xiong, Zhi Yu, Jing-Lin Zuo and Xiao-Zeng You*

Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210008, P. R. China

Xiao-Ying Huang

State Key Laboratory of Structure Chemistry,Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, 350002, P. R. China

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Abstract-Three one-dimension chain adducts,catena-poly- {bis(dibutyldithiophosphato-K^2S,S') nickel(II)-μ-(4,4'-bipyridine)-KN,KN},catena-poly{bis(8-quinolinolato-N^1,O^8)nickel(II)-μ-(4,4'-bipyridine)-KN,KN} and catena-poly{bis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato-K^2O,O') nickel(II)-μ-(4,4'-bipyridine)-KN,KN},hereafter abbreviated to $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$, $[4,4'\text{-}(bipy)\text{-}NiQ_2]_n$ and $[4,4'\text{-}(bipy)\text{-}Ni(TTA)_2]_n$ have been synthesized and characterized by elemental analysis,IR, magnetic properties and X-ray photoelectron spectra(XPS). The crystal structure determination of $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$ reveals that the local coordination geometry around nickel(II) is a distorted octahedron and the $Ni(Bu\text{-}dtp)_2$ units are bridged by 4,4'-bipyridine to form an infinite chain. The Ni-S and Ni-N bond lengths are 2.468(6)-2.494(6)Å and 2.10(2)-2.15(2)Å, respectively.

*Author to whom correspondence should be addressed.

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Introduction

The nickel(II) complexes of dialkyldithiophosphate(dtp), 8-quinolinol(Q) and 2-thienyltrifluoroacetone(TTA) are widely used as lubricating oil and rubber industry additives and a fire-resistant additive for olefin polymers as well as a fungicide for leather[1-4].Recently,their adducts with neutral nitrogen have also attracted broad attention due to their potential applications in petroleum industry[5-7].Futhermore,one-dimension transition metal complexes bridged by bidenate π electron-containing ligands, such as pyrazine and 4,4'-bipyridine(bipy),have gained more importance owing to their potential utilization as organic conductors and magnetic materials[8].To our knowledge, none of the adducts of $Ni(Bu\text{-}dtp)_2$, NiQ_2 and $Ni(TTA)_2$ with 4,4'-bipy has been reported in recent literature.We report here their IR, XPS and magnetic Properties as well as the X-ray crystal structure determination of $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$.

Experimental

Synthesis

1. [4,4'-(bipy)-Ni(Bu-dtp)$_2$]$_n$:Bis(O,O'-dibutyldithiophosphato) nickel(II)($Ni(Bu\text{-}dtp)_2$) was prepared according to the literature method[2]. 4,4'-Bipyridine(analytic grade) was directly used without further purification. $Ni(Bu\text{-}dtp)_2$ (1mmol) was dissolved in EtOH and 4,4'-bipy was also dissolved in EtOH. The two solution were mixed, immediately giving green crystal precipitate. The crystal were collected by filtration, washed with EtOH and dried in vacuo;yield: 98%. Found: C: 44.81, H: 6.42, N: 4.12. Calcd. for $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$: C: 44.73, H: 6.31, N: 4.01.The green needles crystal suitable for X-ray structure analysis were recrystallized from toluene. The toluene solution containing$[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$ evaporated at room temperature for a few weeks to give green needles crystals.

2. [4,4'-(bipy)-NiQ$_2$]$_n$: Bis(8-quinolinolato-N^1,O^8)nickel(II).$2H_2O$ was prepared according to the literature method[6]. $NiQ_2.2H_2O$(1mmol) was dissolved in EtOH and $CHCl_3$ and 4,4'-bipy was dissolved in EtOH. The two solution were mixed for 30 minutes and brown-yellow crystal precipitate appeared. The crystal were collected by filtration, washed with EtOH and dried in vacuo; yield :85%, found: C:66.56, H: 3.60,N: 11.56. Calcd. for $[4,4'\text{-}(bipy)\text{-}NiQ_2]_n$: C:66.56,H: 3.98, N:11.14.

3.[4,4'-(bipy)-Ni(TTA)$_2$]$_n$: Bis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato)nickel(II) ($Ni(TTA)_2$) was prepared according to the literature method[3]. The following procedure is very similar to that of $[4,4'\text{-}(bipy)\text{-}Ni(Bu\text{-}dtp)_2]_n$. The pale blue crystals were obtained after the mixture of $Ni(TTA)_2$ and 4,4'-bipy. yield: 90%. Found: C:47.30,H:2.30,N:4.50. Calcd for $[4,4'\text{-}(bipy)\text{-}Ni(TTA)_2]_n$: C:47.50, H:2.43, N:4.26.

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Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen were performed on a Perkin-Elemer 240C analyser. The infrared spectra from 4000 to 400 cm^{-1} and far-infrared spectra from 500 to 100 cm^{-1} in polyethylene pellets were obtained with a Nicolet 170SX FT-IR spectrophotometer. Magnetic measurement were carried out on a CHAN-2000 Faraday balance with $Ni(en)_3S_2O_3$ as a standard at 6000G magnetic field. The resulting susceptibility was corrected for underlying diamagnetism. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG ES-CALAB MK-II spectrometer using Mg Kα exciting irradiation. Samples were in powder form on double-sided sticky tape on a double-side silicon metal sample holder. Core level binding energy was measured for Ni, S, P,F, O and N atoms in the sample. Calibration was made using C_{1s} binding Energy 284.3eV.

X-ray Structure Determination

A single crystal with the dimension 1.4×0.1×0.06 mm was selected for X-ray diffraction analysis. Diffraction were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα(λ=0.71069Å) radiation. Crystal data for [4, 4'-(bipy)-Ni(dtp)$_2$]$_n$: $C_{26}H_{44}NiP_2N_2S_4O_4$, Mr = 697.53, triclinic space group P1 (No. 2), a = 13.600(4), b = 16.893(6), c = 8.310(2)Å, α = 97.42(3), β = 103.66(2), γ = 105.18(2) °, V = 1753(1) Å^3, Z = 2, μ = 9.04 cm^{-1}, d_c = 1.32 g cm^{-3}, R = 0.073, Rw = 0.079. A total of 6446 reflections were collected, of which 6161 were unique and 1276 with I≥3σ(I) were used in the refinement. The structure was solved by direct methods using MITHRIL.[9] The heavy atom Ni was located in an E map and the remaining non-H atoms were located using the DIRDIF program.[10] H atoms were placed in geometrically calculated positions with C-H bond length of 0.95Å , but were not included in the refinement. The structure was refined by full-matrix least-squares based on F with weights $w=1/\sigma^2(F)$ and with anisotropic displacement parameters for all atoms. Data collection was obtained using CONTROL software.[11] All caculations were performed on a VAX3100 computer using the TEXSAN program package.[12] The selected bond lengths and angles are listed in Table 1 and 2, respectively. Table 3 includes fractional atomic coordinates and equivalkent isotropic displacement paraments in [4, 4'-(bipy)-Ni(dtp)$_2$]$_n$.Molecular structure showing 30% probability displacement ellipsoids and unit cell packing diagram is depicted in Fig. 1 and Fig. 2.

Supplementary material

Tables containing the atomic coordinates, anisotropic displacement coefficients, calculated H atom coordinates, and calculated and observed structure factors (F_c and F_o) have been deposited to the Editor. The information is available on request from our laboratory.

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Table 1 Selected bond lengths (Å) in $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$

Ni(1)-N(1)	2.10(2)	Ni(1)-N(1a)	2.10(2)
Ni(2)-N(2)	2.15(2)	Ni(2)-N(2b)	2.15(2)
Ni(1)-S(1)	2.468(6)	Ni(1)-S(1a)	2.468(2)
Ni(1)-S(2)	2.494(6)	Ni(1)-S(2a)	2.494(2)
Ni(2)-S(3)	2.471(7)	Ni(2)-S(3b)	2.471(7)
Ni(2)-S(4)	2.478(7)	Ni(2)-S(4b)	2.478(7)
P(1)-S(1)	1.98(1)	P(1)-S(2)	2.00(1)
P(2)-S(3)	1.96(1)	P(2)-S(4)	1.96(1)
P(1)-O(1)	1.56(1)	P(1)-O(2)	1.59(2)
P(2)-O(3)	1.62(2)	P(2)-O(4)	1.66(2)
O(1)-C(31)	1.51(3)	O(2)-C(21)	1.52(3)
O(3)-C(51)	1.06(6)	O(4)-C(41)	1.14(7)

Table 2 Selected bond angles (°) in $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$

N(1)-Ni(1)-N(1a)	180(3)	N(2)-Ni(2)-N(2b)	180(8)
S(1)-Ni(1)-S(2)	82.0(2)	S(3)-Ni(2)-S(4)	82.4(3)
N(1)-Ni(1)-S(1)	90.2(5)	N(1)-Ni(1)-S(2)	90.9(5)
N(1)-Ni(1)-S(1a)	89.8(5)	N(1)-Ni(1)-S(2a)	89.1(5)
N(2)-Ni(2)-S(3)	90.6(5)	N(2)-Ni(2)-S(4)	89.3(6)
N(2)-Ni(2)-S(3b)	89.4(5)	N(2)-Ni(2)-S(4b)	90.7(6)
S(1)-P(1)-S(2)	109.8(4)	O(1)-P(1)-O(2)	94(1)
S(1)-P(1)-O(2)	112.4(8)	S(2)-P(1)-O(1)	112.4(7)
S(3)-P(2)-S(4)	112.4(6)	O(3)-P(2)-O(4)	92(2)
S(3)-P(2)-O(3)	112(1)	S(4)-P(2)-O(4)	112(1)

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Table 3. Fractional atomic coordinates and equivalkent isotropic displacement paramenis in [4,4'-(bipy)-Ni(dtp)$_2$]$_n$.

atom.	x	y	z	B(eq)(Å^2)
Ni(1)	1/2	1/2	1/2	3.3(2)
Ni(2)	0	0	1.0000	4.4(2)
S(1)	0.4107(5)	0.4422(4)	0.1963(7)	4.3(3)
S(2)	0.3761(5)	0.5862(4)	0.4587(8)	4.7(3)
S(3)	-0.1745(6)	-0.0204(5)	0.7982(9)	6.9(3)
S(4)	-0.0543(6)	0.1055(4)	1.1650(9)	6.5(3)
P(1)	0.3268(6)	0.5204(4)	0.2212(8)	5.0(3)
P(2)	-0.1843(8)	0.0637(6)	0.975(1)	7.8(4)
O(1)	0.328(1)	0.578(1)	0.088(2)	6.9(8)
O(2)	0.202(1)	0.475(1)	0.152(2)	7.1(8)
O(3)	-0.292(2)	0.033(2)	1.032(3)	15(2)
O(4)	-0.221(2)	0.141(2)	0.901(4)	15(2)
N(1)	0.388(1)	0.407(1)	0.562(2)	3.3(8)
N(2)	0.074(2)	0.096(1)	0.882(2)	4.5(8)
C(1)	0.340(2)	0.426(1)	0.680(3)	5(1)
C(2)	0.273(2)	0.368(2)	0.737(2)	3(1)
C(3)	0.246(2)	0.282(2)	0.669(3)	5(1)
C(4)	0.289(2)	0.266(1)	0.540(3)	5(1)
C(5)	0.356(2)	0.324(2)	0.487(3)	6(1)
C(6)	0.183(2)	0.219(1)	0.744(3)	4(1)
C(7)	0.117(2)	0.143(2)	0.642(3)	6(1)
C(8)	0.062(2)	0.086(1)	0.719(3)	5(1)
C(9)	0.137(2)	0.167(2)	0.982(2)	4(1)
C(10)	0.193(2)	0.229(1)	0.914(3)	5(1)
C(21)	0.150(3)	0.411(2)	0.244(4)	8.9(9)
C(22)	0.031(4)	0.387(3)	0.182(5)	17(2)
C(23)	0.008(6)	0.464(5)	0.25(1)	29(3)
C(24)	-0.103(6)	0.440(4)	0.238(8)	28(3)
C(31)	0.431(2)	0.638(2)	0.085(3)	6.5(7)
C(32)	0.401(2)	0.681(1)	-0.061(3)	6.3(6)
C(33)	0.499(2)	0.741(2)	-0.070(3)	9.4(9)
C(34)	0.482(2)	0.798(2)	-0.203(4)	10(1)
C(41)	-0.163(6)	0.185(5)	0.85(1)	27(4)
C(42)	-0.209(4)	0.221(3)	0.705(7)	20(2)
C(43)	-0.127(8)	0.288(6)	0.65(1)	32(4)
C(44)	-0.137(7)	0.257(6)	0.51(1)	35(5)
C(51)	-0.302(6)	0.011(4)	1.143(9)	25(3)
C(52)	-0.386(3)	-0.002(3)	1.226(5)	15(1)
C(53)	-0.385(4)	-0.063(3)	1.334(6)	19(2)
C(54)	-0.469(4)	-0.098(3)	1.384(6)	20(2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i . a_j .$

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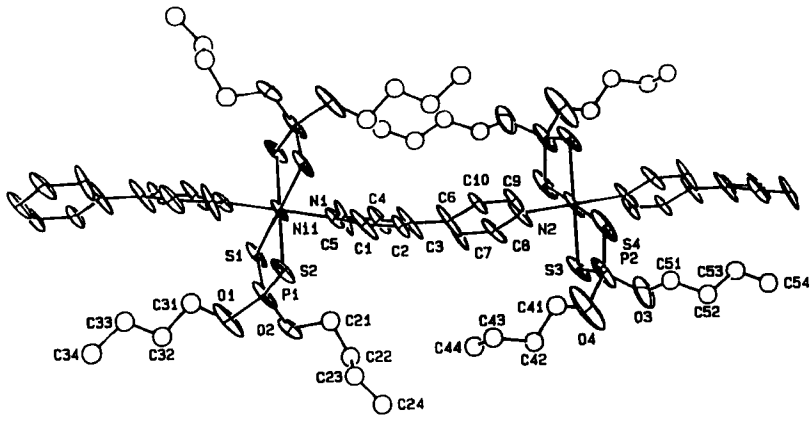

Fig. 1 Molecular structure of $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$ showing 30% probability displacement ellipsoids. H atoms are ommited for clarity

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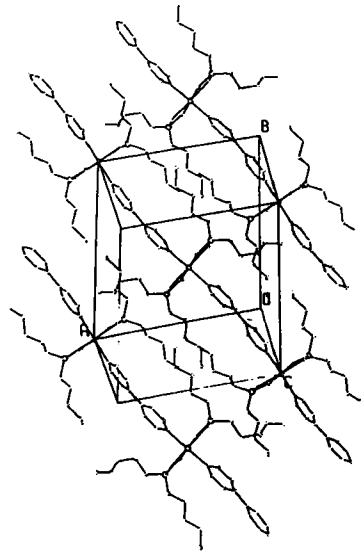

Fig. 2 Perspective view of the unit cell of $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$

Results and Discussion

Spectral features

The results of elemental analysis, IR and far-IR as well as XPS have indicated that the reaction of $Ni(DTP)_2$, NiQ_2 and $Ni(TTA)_2$ with 4,4'-bipyridine yielded the corresponding adducts . IR spectra (see Fig. 3) of $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$ exhibits diagnostic absorption bands of $Ni(dtp)_2$, such as υ_{sym} (Ni-S) (361 cm^{-1}), $\upsilon_{antisym}$ (Ni-S) (325 cm^{-1}),$\upsilon_{antisym}$ (P-S) (658 cm^{-1}), υ_{sym} (P-S) (551 cm^{-1}) and υ_{sym} (P-O) (1027 cm^{-1}, sh) as well as $\upsilon_{antisym}$ (P-O) (970 cm^{-1}), which are consistent with those reported in reference 2. In addition, a strong absorption band with a should peak at 233 and 246 cm^{-1}, respectively are found [13] which may be attributed to the symmetric and antisymmetric Ni-N stretching frequencies, indicating that 4,4'-bipyridine has coordinated to Ni atom, which is confirmed by the results of crystal structure determination as mentioned later. In far-IR spectra of $[4,4'\text{-(bipy)-NiQ}_2]_n$(see Fig.3), three strong absorption which are assigned to νNi-N(228cm^{-1}), νNi-O(300cm^{-1}) and ring deformation(388cm^{-1}) were observed, in agreement with trans-bis(8-quinolinolato)nickel(II)dihydrates but quite different from tetrahedral NiQ_2, indicating that the adduct may be an octahedral geometry. In addition, the absorption bands at 3046(w),1600(m),1570(m),1496(s),1462(s),1363(s),1324(s),1211(m) and 1109(m) cm^{-1} were also observed.

Futhermore,in far-IR spectra of $[4,4'\text{-(bipy)-Ni(TTA)}_2]_n$(see Fig. 3), a strong absorption band at 260cm^{-1} with a should peak (220cm^{-1}) and a medium band at 310cm^{-1} with should peak(330cm^{-1}) may be attributed to the symmetric and antisymmetric stretching mode of Ni-N and Ni-O. A ring deformation vibration mode at 393cm^{-1} was also observed. These characteristic absorption bands are very similar to those of trans-Ni(TTA)2.(3mpy)$_2$.[3] Over the range 800-3200cm^{-1}, the absorption bands at 3074(w), 1604(s), 1536(s), 1413(s), 1353(m), 1303(s), 1231(m),1160(s),1133(s),944(m),860(m) and 820(m) cm^{-1} were found.

It is very interesting to note that in the three adducts, the Ni2p satellites appear very similar (see Fig.4), indicating directly that they have the similar octahedral sterochemistry[6],because the satellites are separated from the corresponding main line by 4-7 eV,i.e.,the metal ions in an octahedral field,the shape-up satellite structure in 2p photoelectron spectra of the transition metal ions should fall in 5-10 eV. It should be pointed out that the other elemental binding energies are unexceptional.

Magnetic property

The room temperature magnetic moments of $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$,$[4,4'\text{-(bipy)-NiQ}_2]_n$ and $[4,4'\text{-(bipy)-Ni(TTA)}_2]_n$ are 3.16 ,3.56 and 2.86 B.M. respectively, in good agreement with the

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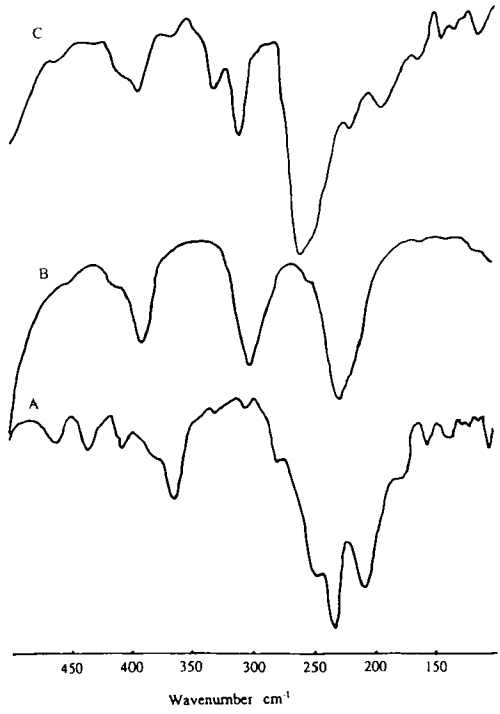

Fig. 3 Far-IR. diagram of $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$ $[4,4'\text{-(bipy)-NiQ}_2]_n$ and $[4,4'\text{-(bipy)-Ni(TTA)}_2]_n$

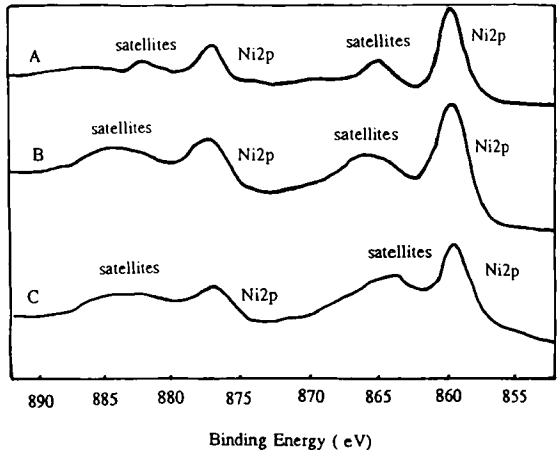

Fig. 4 Typical XPS spectra of the cores levels in the $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$,$[4,4'\text{-(bipy)-NiQ}_2]_n$ and $[4,4'\text{-(bipy)-Ni(TTA)}_2]_n$

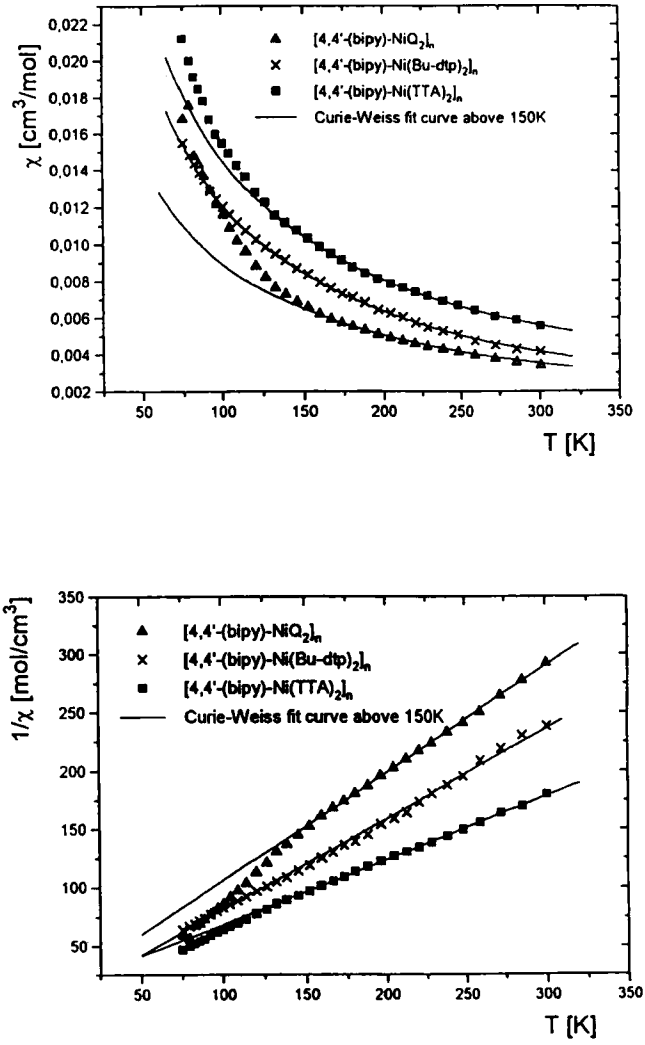

Fig. 5 Inverse molar susceptibility vs temperature for $[4,4'\text{-(bipy)-Ni(Bu-dtp)}_2]_n$ $[4,4'\text{-(bipy)-NiQ}_2]_n$ and $[4,4'\text{-(bipy)-Ni(TTA)}_2]_n$ in the range 75 to 300K

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range normally found for the octahedral nickel (II) complex. The magnetic susceptibility of the adducts as a function of temperature is shown in Fig. 5. The straight line is a least-squares fit to the data over the range 300-150K. The magnetic behavior of the [4,4'-(bipy)-Ni(Bu-dtp)$_2$]$_n$(c=1.203),[4,4'-(bipy)-NiQ$_2$]$_n$(c=1.258) and [4,4'-(bipy)-Ni(TTA)$_2$]$_n$ (c=1.820) obeys the Curie-Weiss Law with X_m=C/(T-θ).The θ values of [4,4'-(bipy)-Ni(Bu-dtp)$_2$]$_n$, and [4,4'-(bipy)-Ni(TTA)$_2$]$_n$ are -32K and -25K, suggesting that in the temperature range 150-300K, the magnetic behavior of the two adducts exhibits weak antiferromagnetic exchange interaction. Similarly,mononuclear adducts of NiA$_2$.2rpic and NiC$_2$.2rpic also display weak antiferromagnetic interaction in the range 14 to 295K[15]. However,the θ value of [4,4'-(bipy)-NiQ$_2$]$_n$ is 10.6K,indicating that its magnetic behavior exhibits weak ferromagnetic exchange interaction,probably due to the presence of the better conjugation effect between 4,4'-bipy ring and metal chelating ring[6].

Crystal structure

The local coordination geometry around the nickel (II) ion is distorted octahedral configuration, in which Ni(Bu-dtp)$_2$ units are linked by 4,4'-bipyridine in a straight fashion with a N(1)-Ni-N(2) angles of 180(3)° to form an infinite chain in the crystal. Two of the these chains pass through a cell in a nearly parallel fashion.

The average Ni-S bond length (2.478 Å) is shorter than those found in the related adducts of Ni(Bu-dtp)$_2$ with nitrogen bases, such as octahedral Ni[(dtp)$_2$·2Py], Ni-S (2.50Å)[16] and trans-octahedral configuration Ni[(dtp)$_2$·2Q], Ni-S (2.513Å),[5] where Ni-N (2.13Å) is in good agreement with those of Ni[(dtp)$_2$·2Py] (2.11Å) and Ni[(Bu-dtp)$_2$·2APy] (2.091(2) Å),[2] (Q=isoquinoline, Apy=4-aminopyridine). On the other hand, the bond angles of S(1)-Ni-S(2) (82.0(2)°) and S(3)-Ni-S(4) (82.4(3)°) are somewhat larger than those of Ni(Bu-dtp)$_2$·2Im (79.44(4)°)[17] and Ni(Bu-dtp)$_2$·2Py (81.51(5)°)[18] (Im=imidazole). It is worthwhile noting that the dihedral angle between the plane of N(1) C(1) C(2) C(3) C(4) C(5) and C(6) C(7) C(8) C(9) C(10) N(2) is quite large (37.52°), showing that the conjugation effects between the two planes may be very weak, leading to the π electron transfer very difficulty. Due to this respect, the magnetic behavior of the title complex may exhibit weak magnetic exchange coupling, which is consistent with the result observed in this work.

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