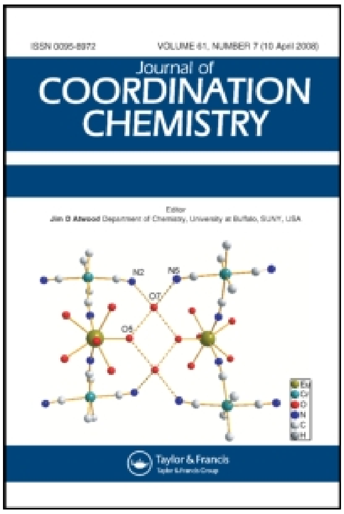

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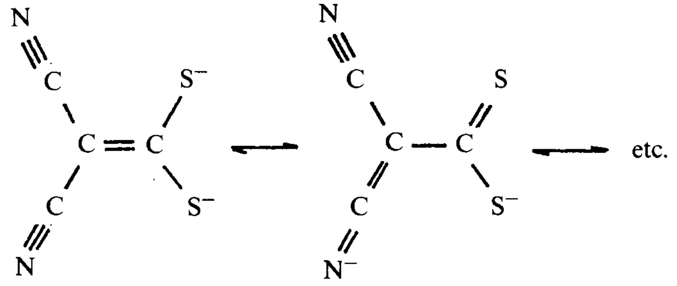
The N1s and S2p core binding energies have been obtained from X-ray photoelectron spectra (XPS) of a series of alkaline earth metal compounds of the ligand 1,1-Dicyanoethylene-2,2-dithiolate (*i*-mnt). The binding energies are effected by various metal cations indicating a polarization effect within the series Ba-Mg. A linear relationship between ν_{CN} and the Nls binding energies was observed. The 01s core binding energies of crystal water in the investigated species have also been obtained. Different bonded water molecules exhibit different binding energies of the 01s electrons. A linear relationship between the temperature of thermal dehydration and the 01s core binding energies has been proposed.

Keywords: Dithiolates, charge density, photoelectron spectroscopy, alkaline earths, binding energies.

INTRODUCTION

In a previous paper[2] we have reported the X-ray photoelectron spectra of the compounds $M(i\text{-mnt})\cdot n\,H_2O$; $M = Mg$, $n = 6$; $M = Ca, Sr$, $n = 5$; $M = Ba$, $n = 3$. From *ab initio* HF-MO calculations it is shown that the negative charge in 'free' *i*-mnt is delocalized and on the S and N atoms in nearly equal amounts.[2]



As XPS provides an extremely powerful tool for investigating the electronic structure of molecules[3] we have decided to study the influences on the charge distribution in *i*-mnt by counter ions in a series of alkaline earth metal salts with well known structural features.[1,4,5] From X-ray structure analyses different bonded water molecules

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TABLE I
Binding energies for N and S atoms in *i*-mnt. Average line-width for S2p is 3 eV, for N1s 2 eV.

Compound	E_b/eV		
	N1s	S2p	Δ(N1s-S2p)
Mg(*i*-mnt)·6H_2O	401.8	164.3	237.5
Ca(*i*-mnt)·5H_2O	402.1	164.7	237.4
Sr(*i*-mnt)·5H_2O	402.6	165.2	237.4
Ba(*i*-mnt)·3H_2O9	403.5	166.2	237.3

$E_b = E_{x\text{-ray}} - E_{kin} - \Phi_{sp}$. $E_{x\text{-ray}}$ = 1486.6 eV (AlKα). ϕ_{sp} = 0.4 eV (C1s *vs* Graphite).

(coordinated to one or two metal cations) have been established. It was expected that different bonded crystal water would show different chemical shifts for the O1s core binding energies.

RESULTS AND DISCUSSION

The chemical shifts of S2p and N1s core binding energies

The sulfur 2p and nitrogen 1s binding energies are listed in Table I for the series of alkaline earth metal salts investigated in the present work.

The binding energy can easily be calculated using the relation[3] $E_b = E_{h\nu} - E_{kin} - \Phi_{sp}$, where $E_{h\nu}$ = incident photon energy, E_{kin} = kinetic energy of the photoelectron as it enters the spectrometer chamber and Φ_{sp} = work function of the spectrometer material (0.4 eV). The ESCA method has been used to obtain information concerning the aspherical charge distribution about the S and N atoms of the ligand *i*-mnt using the

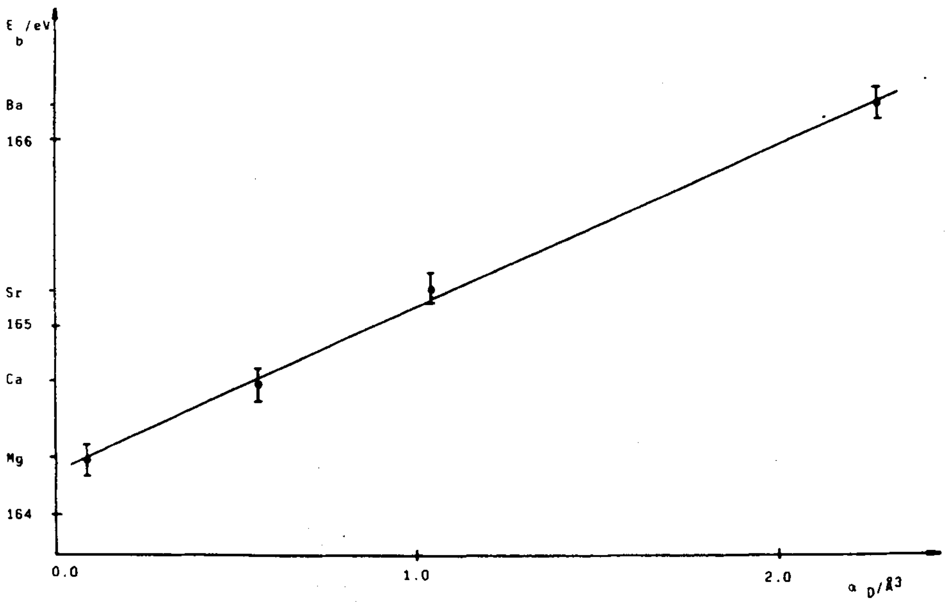


FIGURE 1 Plot of E_b(S2p) energies *versus* α_D (Dipole polarizabilities[9]).

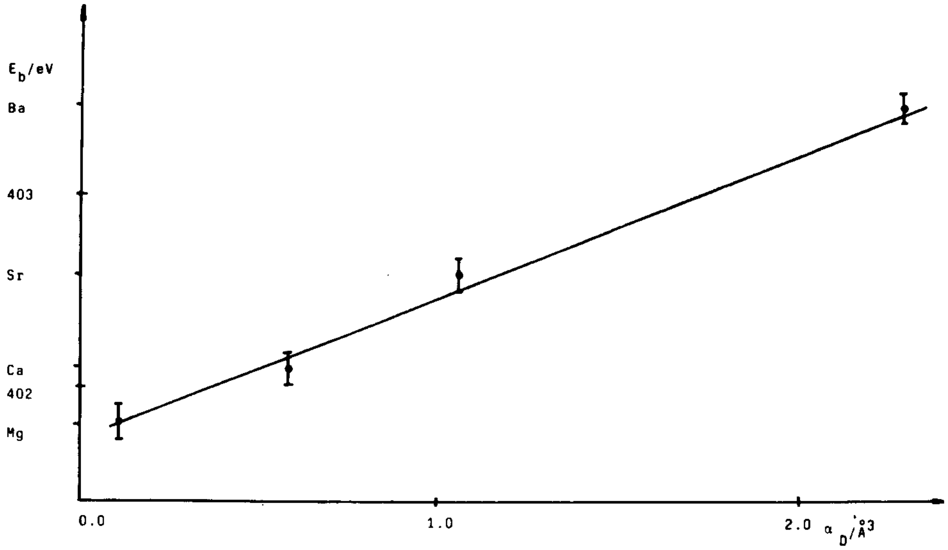


FIGURE 2 Plot of E_b(N1s) energies *versus* α_D (see Fig. 1).

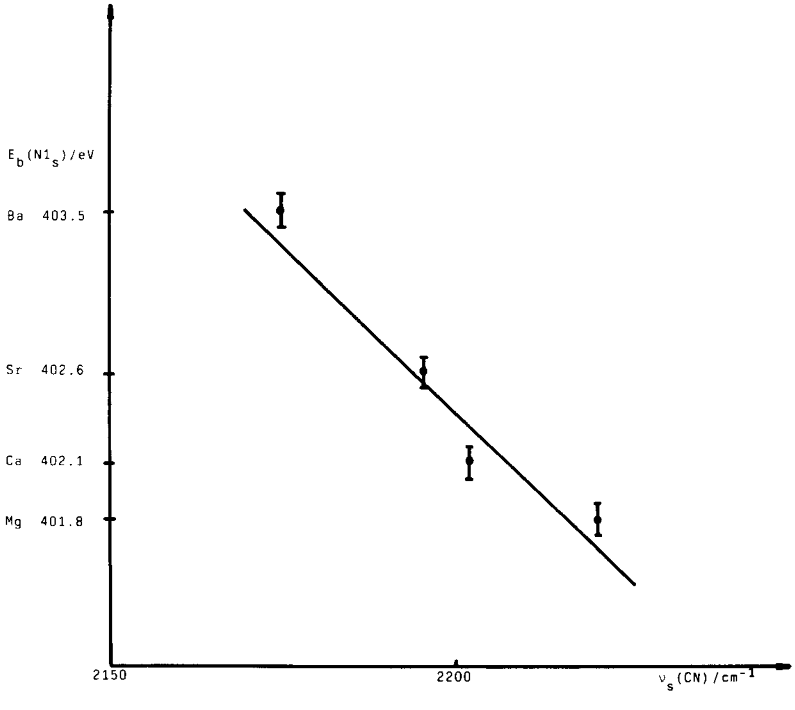


FIGURE 3 Correlation of E_b(N1s) energies with ν_s(CN).

potential model[6,7] with chemical shift, $\Delta E = kq_i + V_i + V'_i + l$, where q_i = atomic charge, $V_i = \Sigma_{i \neq j} q_i/R_{ij}$ (intramolecular potential) V'_i = intermolecular potential and k, l are constants.

The effects of V_i and V'_i on the chemical shifts are expected to be small and are neglected during the following discussion. Taking into account that the reorganization energies of atoms in different molecular sites are quite similar[8] we assume that ΔE is mainly affected by q_i. The intramolecular potentials V_i for *i*-mnt in the known structures remain nearly constant.[2] Additionally, the fact that the Ca and Sr compounds are isostructural may justify the neglecting of V_i and V'_i.

Figures 1 and 2 show the S2p and N1s binding energies for the various compounds *versus* the dipole polarizabilities[9] for the alkaline earth metal cations.

It is obvious that the ligand $(S_2C_4N_2)^{2-}$ is polarized with respect to increasing charge density on the S and N atoms by the metal cations in the order Mg>Ca>Sr>Ba.

In agreement with this, the stretching frequency ν_{CN} for *i*-mnt increases in the order Ba(*i*-mnt)-Mg(*i*-mnt).

Similar results are derived for compounds with SCN^-.[10]

*X-ray structures**

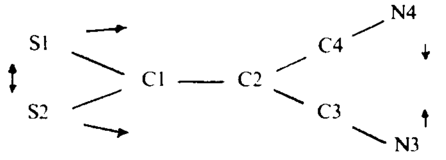
All investigated compounds contain layers of *i*-mnt ligands. Ca(*i*-mnt)·5 H_2O and Sr(*i*-mnt)O·5 H_2O are isotypical. The metal cations have tricapped trigonal prismatic surroundings of 6 0 and 3 N atoms.[1,4] In Ba(*i*-mnt)·3 H_2O Ba is surrounded by 4 0, 3 N and 2 S atoms.[5] In all structures the H_2O molecules are involved in S . . . H hydrogen bonds.

The i-*mnt anions*

It is expected that increased charge on the S atoms leads to an increased S1-C1-S2 angle. As the group $C(CN)_2$ is even more flexible, on increasing charge density on the N atoms the C3-C2-C4 angle will decrease. This trend is obviously seen in the series Ca(*i*-mnt)>Sr(*i*-mnt)>Ba(*i*-mnt) although the effects are small.

TABLE II
The influence of charge density on S and N atoms in *i*-mnt on the molecular framework.

Angle/°	Mg	Ca	Sr	Ba
S1-C1-S2	–	120.4(2)	119.9(4)	119.1(6)
C3-C2-C4	–	113.4(4)	115.5(6)	116.8(1)



The 01s binding energies

Correlations of binding energies and their chemical shifts with physical or chemical parameters such as vibrational frequencies in molecules, cation oxidation states in

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*Although $MgS_2C_4N_2 \cdot 6H_2O$ can be prepared in high purity up to now it was not possible to obtain crystals of sufficient size for X-ray structure analysis.

TABLE III

Binding energies and TG temperatures for the different 0 atoms in alkaline earth compounds of *i*-mnt.

	E_b/eV	$h_{1/2}$	T/°C	H_2O	structural motif/A°	
Ba''	537.2	1.5	219	1	O1-Ba	2.820(7)
						2.866(6)
					-S1	3.162(8)
					-S2	3.222(6)
Ba'	533.7	2.25	136	2		
Sr''	536.2	sh	148.0	1	O2-Sr	2.691(6)
						2.701(4)
					-S1	3.217(6)
					-S1'	3.247(7)
Sr'	533.8	2.25	115.5	4		
Ca	536.3	3.0	130.0	5(?)	O2-Ca	2.512(3)
						2.524(4)
					-S1	3.288(3)
					-S1'	3.214(3)
Mg'''	535.0	1.20	134.0	2		not assigned
Mg''	533.5	sh	105.5	2		
Mg'	531.1	1.05	90.5	2		

$h_{1/2}$: line-width at half height. AlKα radiation with $E_{x\text{-ray}} = 1486.6$ eV.

metal oxides, oxidation number and d-orbital occupancy, Mössbauer isomer shifts etc. have been established.[11]

In the present study we correlate the 01s binding energy of crystal water with the temperature of the thermal dehydration process. Thermal dehydration of the Mg, Sr and Ba salts proceeds in different steps at distinct temperatures. In accordance with this behaviour there are different signals for 01s in the XPS spectra of the compounds which

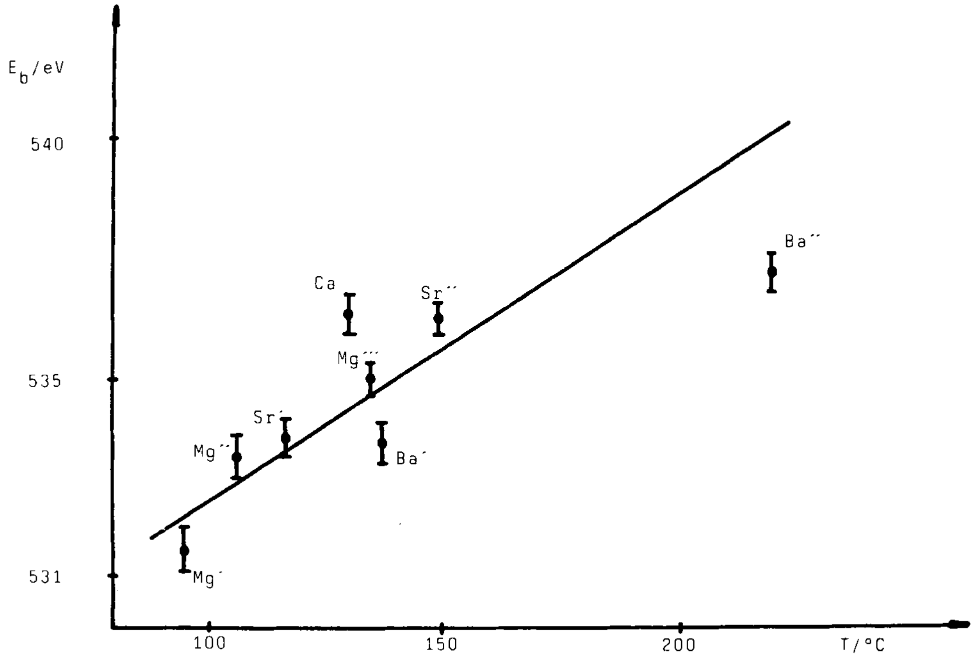

FIGURE 4 Correlation of E_b(01s) energies with thermal dehydration processes.

clearly reflect the existence of different bonded water molecules. It is assumed that an increased 01s binding energy correlates with an increased temperature of water loss in TG studies.

Although in $CaS_2C_4N_2 \cdot 5\ H_2O$ there are two types of H_2O molecules, coordinated with one or two Ca^{2+} respectively, there is only one dehydration step and one broadened 01s signal.

EXPERIMENTAL

Materials

Except for Mg(*i*-mnt)·6 H_2O, for the compounds used in this study suitable syntheses, infrared spectroscopic studies and structural work has been reported elsewhere.[1,4,5] $MgS_2C_4N_2 \cdot 6\ H_2O$ can be obtained from a metathetical reaction of $Mg(SCN)_2 \cdot 4\ H_2O$ and K_2(*i*-mnt)·H_2O.

XPS Spectra

The XPS data were obtained with a Leybold-Heraeus photoelectron spectrometer using AlKα radiation (1486.6 eV) and the C1s signal of the sample holder as standard. Operating pressures were typically in the low 10^{-7} torr range. To check the stability of the compounds measurements were made at room temperature as well as at −170°C. No decomposition effects at room temperature were monitored.

In every case only superimposed signals are observed for the S and N atoms. The S2p signals are combination peaks of $S2p_{1/2}$ and $S2p_{3/2}$ with a maximum near $S2p_{3/2}$.

DTA - TG measurements

All analyses were performed with a STA 429 Netzsch, Selb, instrument. A linear temperature scan was applied from 20 to 400°C under an N_2 atmosphere and with a heating rate of 2°C/min. Standards for DTA and TG measurements were Al_2O_3 and $CaC_2O_4 \cdot H_2O$.

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