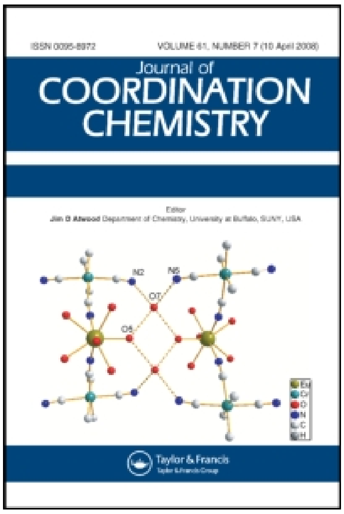

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ESCA OF TETRAAZA MACROCYCLIC COMPLEXES OF SILVER(II)

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To cite this Article Tolentino, Lucio U. and Po, Henry N.(1984) 'ESCA OF TETRAAZA MACROCYCLIC COMPLEXES OF SILVER(II)', Journal of Coordination Chemistry, 13: 4, 341 — 344
To link to this Article: DOI: 10.1080/00958978408073888
URL: http://dx.doi.org/10.1080/00958978408073888

J. Coord. Chem., 1984, Vol. 13, p. 341-344
0095-8972/84/1304-0341 $18.50/0

ESCA OF TETRAAZA MACROCYCLIC COMPLEXES OF SILVER(II)

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(Received November 14, 1983; in final form March 23, 1984)

ESCA results for four tetraaza macrocyclic ligands and their silver(II) complexes have been measured. The Ag 3d binding energies of these complexes fall in the narrow range of 374.3-375.3 eV ($3d_{3/2}$) and 368.2-369.3 eV ($3d_{5/2}$) which are in agreement with the E_b values published previously for silver(II) complexes containing nitrogen donor ligands. Ring substitution with methyl groups has no pronounced influence on the Ag 3d binding energies while ring size variation does cause a small shift in the binding energies. Ring strain energy is invoked as the probable reason for the observed effect.

INTRODUCTION

The technique of ESCA or XPS has been used to study numerous hypervalent silver complexes containing nitrogen donor ligands.[1,2] Of the several known macrocyclic silver(II) complexes only the (*meso*-tetraphenylporphinato)- and the (octaethylporhinato)silver(II) complexes have been studied by this technique.[3] In these studies the silver(II) 3d binding energies have been reported to be in the range of 367-368.5 eV ($3d_{5/2}$) and 373-374.5 eV ($3d_{3/2}$).

In order to obtain an insight as to the effect of the large π ring system of the porphyrin on the silver core electrons binding energies we have decided to examine a series of saturated tetraaza macrocyclic ligands that will form stable complexes with silver(II) and still retain the same geometry of coordination as in the porphinato complexes. Tetraaza macrocyclic complexes of silver(II) can be prepared easily by the disproportionation of silver(I) ions in the presence of the ligands. Using the procedure described by Barefield and Mocella[4] we have prepared four silver(II)-tetraaza macrocyclic complexes and have measured the 3d binding energies of Ag(II) by the ESCA technique. The results are reported herein.

EXPERIMENTAL

Preparation of the Tetraaza Macrocyclic Complexes of Silver(II).

The procedure described by Barefield and Mocella[4] was used in the preparation and recrystallization of four tetraaza macrocyclic silver(II) complexes listed below. These are (*1*): (1,4,8,11-tetraazaacyclotetradecane)-silver(II) perchlorate, $[Ag^{II}[14]aneN_4](C10_4)_2$; (*2*): (1,4,8,12-tetraazacyclopentadecane)-silver(II) perchlorate, $[Ag^{II}[15]aneN_4](C10_4)_2$; (*3*): (meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) perchlorate, $[Ag^{II}\text{-mesoMe}_6[14]aneN_4](C10_4)_2$; and (*4*): (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) perchlorate, $[Ag^{II}[14]ane(NMe)_4](C10_4)_2$.

ESCA Instrumentation

ESCA spectra were measured on a GCA/McPherson ESCA 36 X-ray photoelectron spectrometer equipped with a Siegbahn type electrostatic analyzer using Mg K^{α}

TABLE I
ESCA results for the Silver(II) Tetraaza Macrocyclic ligands and their complexes[a]

Compounds	$3d_{5/2}$	$3d_{3/2}$	N 1s
1 Ag[14]aneN_4 perchlorate	368.2(1.8)	374.3(1.8)	399.4 401.4(s)
2 Ag[15]aneN_4 perchlorate	369.3(1.9)	375.3(1.9)	400.2 402.2(s)
3 Ag-mesoMe_6[14]aneN_4 perchlorate	368.9(2.0)	374.9(2.0)	399.5 401.5(s)
4 Ag-[14]ane$(NMe)_4$ perchlorate	368.0(2.3)	374.2(2.4)	399.2
5 [14]aneN_4			398.4
6 [15]aneN_4			399.0
7 *Meso*-Me_6[14]aneN_4			398.6 400.8(s)
8 [14]ane$(NMe)_4$			398.9

[a] Values in parenthesis are FWHM (full width at half maximum); (s) denotes shake-up satellite peak; average deviation of E_b measurements is ±0.1 eV.

radiation at 1254.6 eV with the power set at 300 watts.[5,6] The sample powders were dusted on double backed sticky tape. In all instances the silver 3d and nitrogen 1s binding energies are referenced to the internal carbon 1s line at 285.0 eV.

RESULTS AND DISCUSSION

Table I summarizes the ESCA results for the tetraaza macrocyclic ligands and their silver(II) complexes. The binding energies of the silver 3d core electrons determined in this study range from 368.2 to 369.3 eV for $3d_{5/2}$ and from 374.3 to 375.3 eV for $3d_{3/2}$. These values are in good agreement with those reported by Kadish and coworkers[3] for porphyrin complexes of silver(II). In making this comparison we have noticed a small difference in the reported binding energies between the two studies. This is confirmed by our measurement of AgOEP[†] (not included in Table I). Our results for the 3d binding energies of AgOEP are 369.2 ($3d_{5/2}$) and 374.9 eV ($3d_{5/2}$). Our values are approximately one eV higher than those reported for the silver(II)-porphyrins in reference (3). This small difference is due to the different reference used by the two studies. Kadish and coworkers used gold $4f_{7/2}$ electrons at 84.0 eV while we used the internal carbon 1s at 285.0 eV for referencing the spectral peaks. Thus the chemical shifts of the silver(II)-porphyrins and the silver(II)-tetraaza macrocyclic complexes are remarkably similar when allowance for the one eV difference is made. This similarity in 3d binding energies suggests that the silver(II) ion in both types of macrocycles must have nearly the same charge intensity in spite of the fact that the tetraaza macrocycles are saturated ligands with no macro π ring system.

Murtha and Walton[2] have reported previously that paramagnetic silver(II) complexes exhibit broader 3d peak widths (+.8 eV) than diamagnetic silver(II) complexes. This was attributed to the occurrence of multiplet splittings due to the paramagnetic $4d^9$ silver(II) ion. We have found that the 3d peak widths of the silver(II)-tetraaza macrocyclic complexes range from 1.8 to 2.4 eV and are in agreement with the average value of 2.4 eV reported by Murtha and Walton.[3] This

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[†] The octaethylporphinato complex.

gives further evidence to the finding that peak width broadening is due mainly to the paramagnetic Ag(II) ion and not to the type of ligands in the coordination sphere.

The effect of ring size on 3d binding energies is shown in Ag^{II}-[15]aneN_4 which has (0.4 to 1.2 eV) E_b values higher than the corresponding [14]aneN_4 complexes (*1,3 and 4*). This difference is presumably due to the difference in ring strain energies between these complexes. The relationship between ring size of tetraaza macrocycles and metal-donor distance has been demonstrated by Busch and coworkers.[5,6] They have shown that there is an ideal ring size (metal-donor distance) for a given metal ion such that ring strain will be minimized. That is to say, the metal ion must have a given metal-donor distance slightly smaller (0.1-0.2 Å) than the ideal ring size of the macrocycle. Based on this assumption, it appears that [15]aneN_4 is the macrocycle that would accommodate silver(II) with the least ring strain since the known crystallographic Ag-N distance[7] is about 0.07-0.12 Å smaller than the ideal ring size of [15]aneN_4 (2.23 to 2.28 Å).[6]

The nitrogen 1s peak of three Ag^{II}- tetraaza macrocyclic complexes (*1, 2 and 3*) exhibits shake-up satellite structures approximately 2 eV higher in binding energy. Shake-up satellites in ESCA spectra have been the subject of numerous studies.[8-10] Electronic phenomena as well as structural variations such as a change in coordination geometries of the transition metal complexes were proposed to explain the occurrence of the shake-up satellites. The latter can be verified using structural information derived from X-ray crystallography studies of the silver(II) complexes. Evidence from crystallographic studies on Ag^{II}-*meso*-Me_6[14]aneN_4 nitrate[7] and Ag^{II}[14]aneN_4 perchlorate[11] have shown that silver(II) is at the center of a square plane surrounded by four nitrogens with an average Ag-N distance of 2.160(3) Å. In the crystallographic study of Ito and co-workers,[11] it was shown that 25% of Ag^{II}[14]aneN_4 perchlorate has the silver(II) ion 0.24 Å below the plane formed by the four nitrogens and the average Ag-N distance is 2.192 Å. The existence of two environments in the crystal structures of reference (11) may be the result of perchlorate being the counter ion rather than nitrate since the complex with the latter anion gave only one Ag-N bond distance.[7] Nevertheless, this variation might be the reason why some of our silver(II)-tetraaza macrocyclic complexes exhibit N 1s shake-up satellite peaks. Other electronic phenomena proposed in related studies can be just as likely and cannot be ruled out.[8-10] Other than the shake-up peaks the major nitrogen 1s peaks of the saturated tetraaza macrocyclic complexes occurred at about the same E_b values as those of the silver(II)-porphyrins and other related metalloporphyrins.[12]

ACKNOWLEDGEMENTS

We wish to thank the Aerospace Corporation for the use of the ESCA spectrometer. This work is supported in part by a grant-in-aid from the University Research Committee.

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