# Reactions of Cadmium(II) Acetate with Acetoacetanilide and Methylacetoacetate Thiosemicarbazones: A Cyclization Process Leading to a Pyrazolone − The Molecular and Crystal Structures of the Free Ligands and the Complex [$CdL_2Py$] (HL = 2-[Amino(thioxo)methyl]-5-methyl-2,3-dihydro-1*H*-3-pyrazolone, Py = Pyridine)

**José S. Casas,[a] María V. Castaño,*[a] Eduardo E. Castellano,[b] María S. García-Tasende,[a] Agustín Sánchez,[a] María L. Sanjuán,[a] and José Sordo[a]**

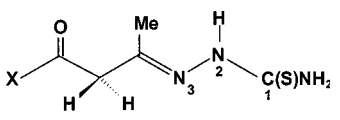
**Keywords:** Cadmium(II) pyrazolonates / Thiosemicarbazones / Cyclizations / 2-[Amino(thioxo)methyl]-3-pyrazolone / $^{1}$H-, $^{13}$C-, $^{113}$Cd-NMR spectra

Acetoacetanilide- and methylacetoacetate thiosemicarbazones (HTSC$^{1}$ and HTSC$^{2}$, respectively) react with cadmium(II) acetate in methanol, giving complexes containing the ligand 2-[amino(thioxo)methyl]-5-methyl-2,3-dihydro-1*H*-3-pyrazolonate ($L^-$). An X-ray diffraction study of the structures of HTSC$^{1}$, HTSC$^{2}$, HL, and [$CdL_2Py$], identified the main structural changes in the cyclization process. Additionally, the coordination of the metal in the complexes [CdL(AcO)] · 2 MeOH and [$CdL_2$] · 3 $H_2O$ was analyzed using IR spectroscopy in the solid state and $^{1}$H-, $^{13}$C-, and $^{113}$Cd-NMR spectroscopy in solution. On reaction with aqueous trifluoroacetic acid, both complexes releases the free pyrazolone, which can be easily isolated.

Cadmium is an environmental pollutant of worldwide concern. In most studies of its interaction with natural or man-made chelating agents, the products, complexes with a wide range of coordination spheres[1] and stabilities,[2] have shown no regiochemical modification of the ligand. We report here two cases of complexation involving cyclization of the ligand.

In spite of the frequent use of thiosemicarbazones (HTSCs) as ligands, mainly with transition metals,[3] only six complexes of HTSCs with cadmium have been fully identified by X-ray diffraction: namely, five adducts of cadmium with neutral HTSC and halide ligands[4] and the complex [$Cd(TSC)_2$] ($TSC^-$ = pyridine-2-carbaldehyde thiosemicarbazonate).[4a] These six compounds exhibit a surprising range of coordination numbers (4, 5, 6, and 7) and coordination polyhedra (tetrahedral, bipyramidal trigonal, highly distorted octahedral and distorted bipyramidal pentagonal).[4]

As part of our work in this field, we recently prepared some HTSCs derived from β-keto esters and β-keto amides (**I**) and reacted them with cadmium(II) acetate in methanol solution. In view of the previous work of Jayasree and Aravindakshan,[5] we expected to obtain cadmium(II) complexes of the mono- or bi-deprotonated ligands, with or without an accompanying acetate ligand. Instead, we obtained new $Cd^{II}$ compounds containing, in deprotonated form, the ligand 2-[amino(thioxo)methyl]-5-methyl-2,3-dihydro-1*H*-3-pyrazolone (HL, **II**).

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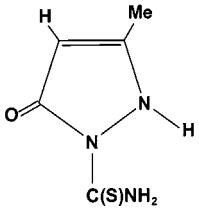


(II)

The new pyrazolonate complexes [CdL(OAc)] · 2 MeOH and [$CdL_2$] · 3 $H_2O$ are interesting for at least two reasons. Firstly, under acidic conditions they release the free pyrazolone; thus, reaction of this type of HTSC with $Cd^{II}$ acetate and subsequent acidification, constitutes a means of obtaining good yields of compounds that are of great interest in organic, biological, pharmaceutical, analytical and agricultural chemistry.[6] Secondly, these cadmium(II) pyrazolonates appear to be the first to have been characterized by X-ray diffraction. In this paper we suggest a plausible reaction pathway and describe the structural characterization of the complexes in the solid state and in solution.

## Results

### Synthesis of the Complexes

The analytical, spectroscopic, and structural data (vide infra) suggest that the HTSC molecules may be transformed into the final pyrazolonate ligand ($L^-$) via the reaction

[a] Departamento de Química Inorgánica,
Universidade de Santiago de Compostela,
15706 Santiago (A Coruña), Spain
E-mail: qitoyi@usc.es
[b] Instituto de Física de Sao Carlos, Universidade de Sao Paulo
Caixa Postal, 369, CEP 13.560, Sao Carlos, SP, Brazil
E-mail: pino@ifqsc.sc.usp.br

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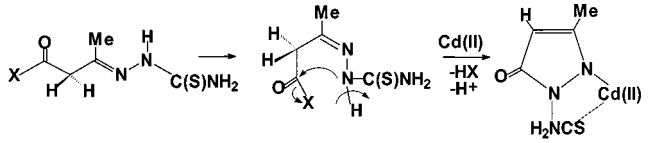
pathway shown in Scheme 1. This pathway is similar to that described by Katrizky et al.[7] for the condensation of a β-ketoester with hydrazine (Knorr′s synthesis of 2,4-dihydro-3*H*-pyrazol-3-ones).

The cyclization, with concomitant elimination of HX (= aniline in HTSC[1] and methanol in HTSC[2]) seems to be favoured by the $Cd^{II}$ cation, possibly because the cadmium(II) thiosemicarbazonate is formed first, deprotonating N(2) and so favouring nucleophilic attack by N(2) on the −C(O)X group.




Scheme 1. Proposed cyclization mechanism

This reaction is related to those investigated by S.A. Samath et al.,[8] who found that β-ketoester complexes of $Cu^{II}$ incorporated phenylhydrazine into the coordination sphere of the metal after a condensation/elimination reaction with the β-ketoester, and that cyclization to pyrazolones occurred upon subsequent demetallation with $H_2S$. In the reaction of HTSC[1] and HTSC[2] with $Cd^{II}$, the elimination/cyclization processes is so favoured that no thiosemicarbazonate intermediates were isolated at room temperature. The cadmium(II)-induced process is also related to previously described cyclizations of aldehyde thiosemicarbazones,[9] but differs from these latter examples in that it seems to involve no change in the oxidation state of the metal.

## Structures of the Ligands

The numbering scheme used for the ligands are shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

The bond lengths in the thiosemicarbazone ligands indicate the double bond character of C(5)−O [C(5)−O(2) in HTSC[2]], C(2)−N(3), and C(1)−S. In accordance with the canonical forms associated with the TSC chain[10] this also suggests some multiplicity in C(1)−N(2) and C(1)−N(1). In HTSC[1] the SC(1)N(1)N(2)N(3)C(2)C(3)C(4) and C(6)C(7)C(8)C(9)C(10)C(11)N(4) moieties are both planar (Rms. = 0.028 and 0.010, respectively) and form a dihedral angle of 67.9°; C(5) and O lie outside these planes. In HTSC[2] too, most atoms lie in one of two, almost orthogonal planes (dihedral angle 85.8°), one containing the TSC backbone [SN(1)C(1)N(2)N(3)C(2), Rms. = 0.019] and the other containing the non-thiosemicarbazone moiety C(4)C(5)O(1)O(2)C(6) (Rms. = 0.007); in this case C(3) lies outside these planes. In both HTSC[1] and HTSC[2], the configuration of the thiosemicarbazone chain is, as usual in this type of compound, (*E*) with respect to the C(2)−N(3) (aldimine) bond, and the thioamide S and N(3) atoms are mutually *trans* with respect to the C(1)−N(2) bond. This latter arrangement allows the formation of a strong intra-

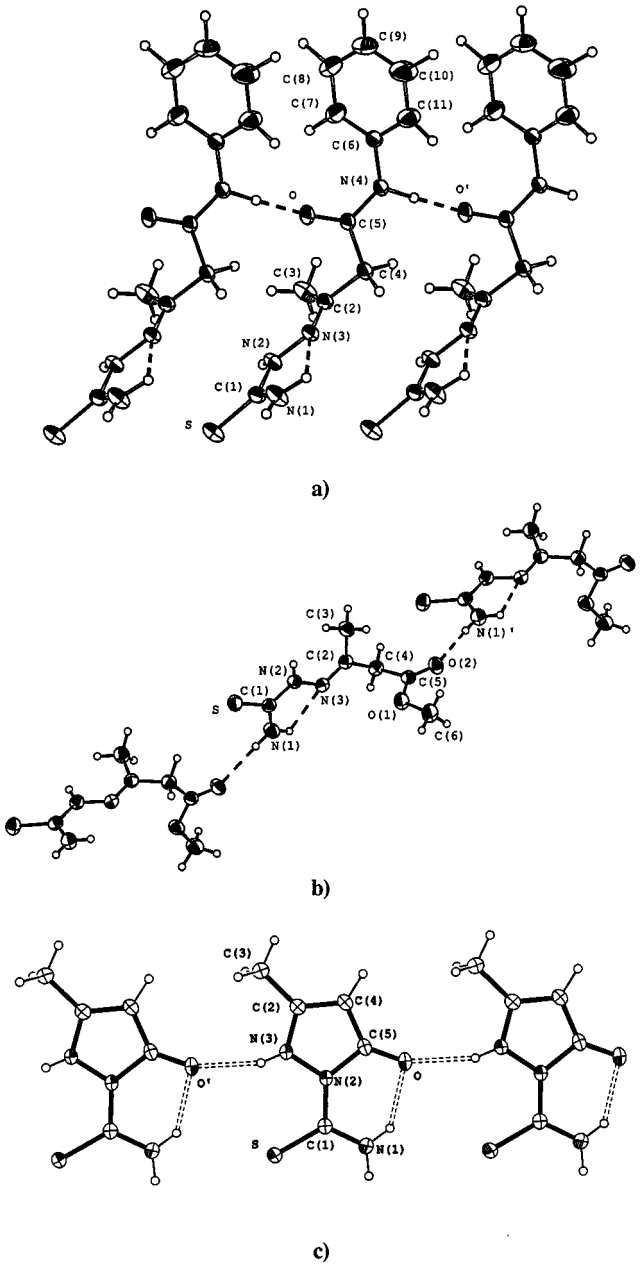



Figure 1. Crystal structures (with 30% probability ellipsoids) of a) HTSC[1], b) HTSC[2] and c) HL, showing intra- and intermolecular hydrogen bonds

molecular hydrogen bond between N(1)−H and N(3) (Figure 1, Table 1), which must aid the partial multiplicity of C(1)−N(1) bond in restricting rotation of the $-NH_2$ group in solution (vide infra NMR data). As Figure 1 and Table 1 show, there is also an intermolecular hydrogen bond between the carbonyl oxygen and N(4) (in HTSC[1]) or N(1) (in HTSC[2]), and this links the molecules in the lattice.

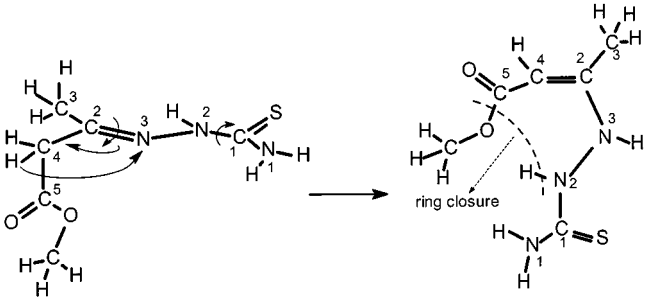
The formation of HL from these HTSC ligands implies that significant structural rearrangement occurs. The steps hypothesized are (Scheme 2): i) a 180° rotation about the C(1)−N(2) bond (as usually occurs when thiosemicarbazonates coordinate to a metal ion);[11] ii) a rotation about the C(2)−N(3) bond (by 67.9 and 85.8° in HTSC[1] and

Table 1. Selected bond lengths [Å] and angles [°]

| Atom 1 | Atom 2 | Atom 3 | HTSC[1] | HTSC[2] | HL | $CdL_2Py$[a] |
|---|---|---|---|---|---|---|
| S | C(1) | | 1.689(5) | 1.685(3) | 1.670(2) | 1.698(4)/1.703(4) |
| N(1) | C(1) | | 1.311(7) | 1.325(4) | 1.318(3) | 1.314(5)/1.306(5) |
| C(1) | N(2) | | 1.354(6) | 1.341(4) | 1.382(2) | 1.369(5)/1.368(5) |
| N(2) | N(3) | | 1.387(5) | 1.383(3) | 1.376(2) | 1.383(5)/1.390(5) |
| N(3) | C(2) | | 1.272(6) | 1.268(4) | 1.377(3) | 1.324(6)/1.329(6) |
| C(2) | C(4) | | 1.502(7) | 1.507(4) | 1.376(3) | 1.393(7)/1.378(7) |
| C(4) | C(5) | | 1.527(6) | 1.517(4) | 1.409(3) | 1.382(7)/1.377(7) |
| C(5) | O[b] | | 1.216(6) | 1.191(4) | 1.240(2) | 1.258(5)/1.265(5) |
| C(1) | N(2) | N(3) | 117.2(4) | 118.8(2) | 121.77(15) | 122.0(3)/122.1(3) |
| N(2) | N(3) | C(2) | 117.7(4) | 119.0(2) | 108.6(2) | 105.0(3)/104.7(3) |
| N(3) | C(2) | C(4) | 115.6(4) | 116.0(3) | 109.8(2) | 112.5(4)/112.6(4) |
| N(1) | N(3) | | 2.594(4) | 2.617(4) | | |
| O(1) | N(1) | | | | 2.669(3) | 2.625/2.618 |
| N(4) | O[i,c] | | 2.861(5) | | | |
| O(1) | N(1)[ii] | | | 3.012(4) | | |
| O(1) | N(3)[iii] | | | | 2.778(2) | |
| N(1) | O(2)[iv] | | | | | 2.822 |
| N(4) | O(1)[v] | | | | | 2.821 |

[a] Values for the two $L^-$ ligands. – [b] Carbonyl group distance. – [c] Symmetry operation: i) $x-1, y, z$; ii) $x+1, 1.5-y, z-0.5$; iii) $x-1, y, z$; iv) $-x, 0.5+y, 0.5-z$; v) $0.5+x, 1.5-y, -z$.

HTSC[2], respectively) so as to make the TSC and non-TSC moieties almost coplanar; iii) displacement of the double bond from C(2)–N(3) to C(2)–C(4) with simultaneous proton transfer from C(4) to N(3); and iv) deprotonation of N(2)–H, elimination of HX, and ring formation. This sequence of changes is in keeping with the following observed changes in bond lengths and bond angles: a) shortening of the C(2)–C(4) bond (which formally becomes a double bond), shortening of the C(4)–C(5) bond [which probably becomes involved in charge delocalization between O and C(5)] and lengthening of the C(2)–N(3) bond (which formally changes from double to single); b) narrowing of the [N(2)–N(3)–C(2)] and [N(3)–C(2)–C(4)] angles and widening of the [C(1)–N(2)–N(3)] angle, which are all affected by ring closure; and c) narrowing of the N(1)–C(1)–N(2) angle, possibly due to the strong intramolecular hydrogen bond –NH···O=C that is present in the cyclic compound (see Table 1). An intermolecular hydrogen bond between the carbonyl oxygen and the N(3)–H group of a neighbouring molecule is also shown in Figure 1 and Table 1.




Scheme 2. Hypothesized rearrangement of HTSC[2] under cyclization

## Structure of the Complex $[CdL_2Py]$

Recrystallization of $[CdL(OAc)] \cdot 2$ MeOH from pyridine afforded monocrystals of $[CdL_2Py]$ (see Figure 2 for the numbering scheme used). In this complex, the deprotonated ligand coordinates to $Cd^{II}$ via N(3) and the exocyclic S atom, as is usual in thiosemicarbazonates. According to Addison et al's τ-criterion,[12] the value $\tau = 0.63$ means that the coordination polyhedron is closer to a trigonal bipyramid (theoretical $\tau = 1$), with N(3) and N(6) in the apical positions [N(3)–Cd–N(6) = 170.3°], than to a square pyramid ($\tau = 0$). The bond lengths in the $[CdN_3S_2]$ kernel ($Cd-N_{Py}$ = 2.312 Å, average Cd–S = 2.554 Å, average $Cd-N_{TSC}$ = 2.293 Å) are shorter than in all the other cadmium(II) thiosemicarbazone derivatives studied so far,[4] including those in which the pyridine ring is part of the coordinated ligand [$Cd^{II}$-pyridine-2-carbaldehyde thiosemicarbazones[4a] and $Cd^{II}$-2,6-diacetylpyridine monothiosemicarbazone[4b]]. The bond lengths in this kernel are also clearly shorter than those reported for bis(benzothiazole-2-thiolato-*N,S*)bis(pyridine)cadmium(II) $[Cd(C_7H_4NS_2)_2(Py)_2]$,[13] which like $[CdL_2Py]$ contains two N,S-bound rings and coordinated pyridine (although it must be borne in mind that $[Cd(C_7H_4NS_2)_2(Py)_2]$ contains two mol of Py and its cadmium has a coordination number of six). In fact, the $Cd-N_{Py}$ distance is close to the minimum value found in the CSD[14] for Cd-pyridine compounds (2.300 Å), and is well below the mean, 2.355 Å. These data suggest strong metal-ligand interaction.

As in the free ligand, the pyrazolone rings are planar [Rms. = 0.009 and 0.010 for N(2)N(3)C(2)C(3)C(4)-C(5)O(1) and N(5)N(6)C(7)C(8)C(9)C(10)O(2), respectively] but upon coordination undergo certain structural changes that are worth mentioning. The C–S bond lengthens, though the fact that the lengthening is less than in the $Cd^{II}$ complex of deprotonated pyridine-2-carbaldehyde

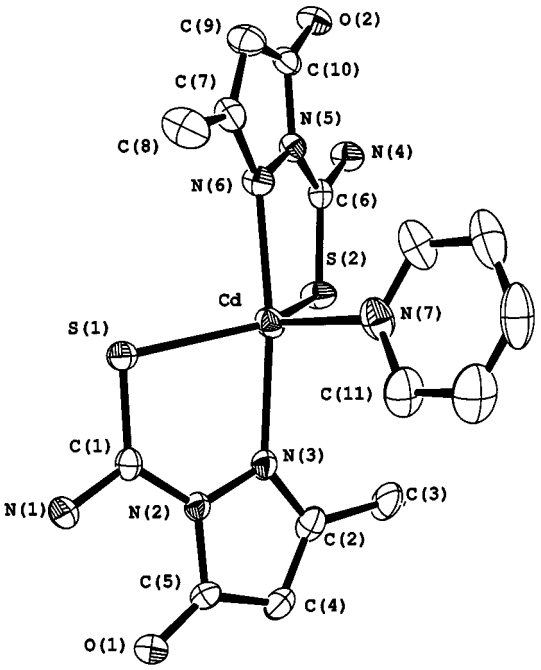



Figure 2. Molecular structure of $[CdL_2Py]$ (with 30% probability ellipsoids); selected bond lengths [Å] and angles [°]: Cd−S(1) 2.5546(11), Cd−S(2) 2.5540(11), Cd−N(3) 2.294(3), Cd−N(6) 2.292(3), Cd−N(7) 2.312(4), S(1)−Cd−S(2) 132.43(5), S(1)−Cd−N(3) 77.50(9), S(1)−Cd−N(6) 98.59(9), S(1)−Cd−N(7) 113.74(10), S(2)−Cd−N(3) 98.48(9), S(2)−Cd−N(6) 77.53(9), S(2)−Cd−N(7) 113.83(11), N(3)−Cd−N(6) 170.35(13), N(3)−Cd−N(7) 95.0(2), N(6)−Cd−N(7) 94.7(2)

thiosemicarbazone[4a] shows that there is less thione-to-thiol evolution in the pyrazolone compound. The associated shortening of the C(1)−N(2) bond is correspondingly slight, suggesting that the multiplicity of this bond increases only slightly upon coordination of the ligand to cadmium. The evolution of the bond lengths in the O(1)−C(5)−C(4)−C(2) and O(2)−C(10)−C(9)−C(7) pyrazolonato moieties [shortening of the C(4)−C(5)/C(9)−C(10) bonds and lengthening of the O(1)−C(5)/O(2)−C(10) and C(2)−C(4)/C(7)−C(9) bonds] is indicative of π-charge delocalization in this part of the ring upon metallation of nitrogen.

In $[CdL_2Py]$ the intramolecular $-NH_2\cdots O$ hydrogen bond is somewhat shorter than in the free ligand (2.625 Å). Four intermolecular hydrogen bonds involving the $-NH_2$ groups and the carbonyl O atoms connect the molecules of the complex in a three-dimensional network.

## IR Spectroscopy

The significant IR bands of $HTSC^1$ and $HTSC^2$ (Experimental Section) were identified on the basis of previous data.[4a,5,15,16] Bands due to the $-N(H)C_6H_5$ and $-OCH_3$ groups were lost upon cyclization (this is more evident for $HTSC^1$ than $HTSC^2$, the $-OCH_3$ bands of which overlap those of the thiosemicarbazone fragment).

The N,S-coordination of the ligand $L^-$ in $[CdL_2Py]$, shown by X-ray diffraction (vide supra), does not significantly shift the ring bands from their positions in the spectrum of free HL, but does shift the low-energy ν(C=S) band to lower wavenumbers and suppresses the high-energy band. The C=O group is non-coordinated, but is strongly involved in hydrogen bonds, which, together with the electronic reordering consequent on deprotonation and *N*-metallation, shift ν(C=O) to lower wavenumbers than in the spectrum of HL.

The positions of the main ring bands and ν(C=S) suggest that $L^-$ is also N(3),S-coordinated in $[CdL(OAc)]\cdot 2\,MeOH$ and $[CdL_2]\cdot 3\,H_2O$. However, the larger shift in ν(C=O) suggests that this group is also Cd-coordinated in these two compounds. This would reduce the involvement of the −C=O group in strong hydrogen bonds with the $NH_2$ group, and might therefore explain why ν(N−H) lies at higher wavenumbers than for $[CdL_2Py]$. It thus seems reasonable to hypothesize that both $[CdL_2]\cdot 3\,H_2O$ and $[CdL(OAc)]\cdot 2\,MeOH$ have polymeric structures, with Cd hexacoordinated in an $N_2S_2O_2$ kernel in $[CdL_2]\cdot 3\,H_2O$, and pentacoordinated in an $NSO_3$ kernel in $[CdL(OAc)]\cdot 2\,MeOH$. The acetate anion in the latter complex is likely to be bidentate (it is difficult to draw this conclusion with certainty from the difference between $\nu_{as}$(COO) and $\nu_s$(COO) because of the breadth of the bands at 1602 and 1399 $cm^{-1}$, to which $\nu_{as}$(COO) and $\nu_s$(COO) must contribute[17]).

## NMR Spectroscopy

The $^1H$ NMR spectra of $HTSC^1$ and $HTSC^2$ show two groups of signals for each of the groups $-N(1)H_2$, $-N(2)H$, $-C(2)H_3$, and $-C(4)H$, indicating that there is probably more than one conformer in solution (only signals for the major conformer are indicated in the Experimental Section). Signals for $-OCH_3$ and $-HNC_6H_5$ are also observed. The $^1H$-NMR spectrum of HL differs markedly from those of its precursors: the signals of $-N(H)C_6H_5$ and $-OCH_3$ are missing, the −NH and $-CH_3$ protons are more deshielded, and there is a new signal at δ = 5.16 corresponding to the $-C(4)H$ group left upon loss of a proton by $-C(4)H_2$ in the cyclization process.

The $^1H$-NMR spectra of the $Cd^{II}$ complexes obtained by reaction of $HTSC^1$ and $HTSC^2$ with $Cd^{II}$ acetate provided the first evidence of the cyclization of these ligands. They show no $-N(H)C_6H_5$ or $-OCH_3$ signals, and instead show a new signal at about δ = 4.7 which corresponds to the −CH signal latter observed at δ = 5.16 in the spectrum of HL. In view of this, the reaction was followed spectroscopically at room temperature by running spectra of a 2:1 $HTSC^1/Cd(OAc)_2$ mixture in DMSO. The spectrum of the freshly prepared mixture shows signals suggesting the initial formation of the complex $[Cd(TSC^1)_2]$, since only the signal of the $-N(2)H$ proton is missing. The spectrum recorded 12 h later contains signals corresponding to $[Cd(TSC^1)_2]$ and $[CdL_2]$, and also signals for free aniline [at δ = 7.01(t), 6.57(t), 6.49(d), and 4.99(s)].

Comparison of the $^1$H-NMR spectra of HL and its $Cd^{II}$ complexes shows that coordination led to deprotonation of the ligand, as indicated by loss of the N(3)H signal.

In the $^{13}$C-NMR spectrum, the main effects of coordination are a shielding of C(4) by about 5.5 ppm and a deshielding of C(2) and C(5) by about 4 ppm (Table 2). C(3) is deshielded by about 2 ppm, while the C(1) signal is hardly shifted. These data show that coordination causes only small modifications in the electronic charge distribution of the N(3)−N(2)−C(1)S$NH_2$ fragment, but major modifications in the fragment C(3)−C(2)−C(4)−C(5)−O, in accordance with the X-ray data for [$CdL_2$Py] in the solid state. This suggests that the solid−state coordination mode persists in [$D_6$]DMSO. The virtually constant position of the C(1) signal is attributable to slight shielding [due to some evolution from an N(2)−C(1)=S towards an N(2)=C(1)−S configuration] being offset by the deshielding inductive effect of the metal−sulfur bond.

The $^{113}$Cd-NMR spectrum of [$CdL_2$] · 3 $H_2O$ shows a single signal at δ = 281 (Table 2), which indicates greater shielding than is expected in an [$S_2N_2$] kernel.[18] In fact, even though the shielding of the $^{113}$Cd nucleus generally increases with its coordination number,[19] the signal is even further upfield than in the complex [Cd(TSC)$_2$] (HTSC = pyridine 2-carboxyaldehyde thiosemicarbazone)[4a] which has an [$S_2N_4$] kernel. This probably indicates an increase in coordination number due to coordination to DMSO oxygen atoms. The fact that the $^{113}$Cd chemical shift of [$CdL_2$Py] is exactly the same as that of [$CdL_2$] · 3 $H_2O$, showing Cd to have the same chemical environment in both, therefore suggests that in the former the Py ligand is replaced by molecules of solvent.

Table 2. $^{13}$C- and $^{113}$Cd-NMR chemical shifts (in ppm)

| Compound | δC(1) | δC(2) | δC(3) | δC(4) | δC(5) | δ($^{113}$Cd) |
|---|---|---|---|---|---|---|
| HTSC$^1$ | 178.8 | 148.8 | 16.8 | 46.5 | 167.3 | |
| HTSC$^2$ | 178.9 | 147.2 | 16.8 | 43.7 | 170.1 | |
| HL | 175.8 | 152.7 | 12.1 | 91.4 | 163.3 | |
| [CdL(AcO)] · 2 MeOH | 176.3 | 157.3 | 14.7 | 85.7 | 167.0 | 156<br>286 |
| [$CdL_2$] · 3 $H_2O$ | 176.2 | 156.8 | 14.7 | 86.0 | 166.7 | 281 |
| [$CdL_2$Py] | 176.1 | 156.8 | 14.4 | 85.9 | 166.7 | 281 |

[a] $CH_3COO^-$: 22.1 (Me), 178.0 ($COO^-$).

The $^{113}$Cd-NMR spectrum of [CdL(OAc)] · 2 MeOH shows signals at both δ = 156 and 286 (area ratio 5:1). This suggests the existence of an equilibrium involving at least two species, in which the cadmium atom has different environments. Assuming that the replacement of S and N atoms by O atoms increases shielding,[20] the signal at δ = 156 can probably be assigned to the primary complex [CdL(OAc)], in which the Cd coordination sphere comprises pyrazolone N and S atoms (one each) together with O atoms from the OAc ligand and, probably, from the solvent. The signal at δ = 286, which lies very close to that of [$CdL_2$], may be due to a small amount of the later species being formed upon dissolution of [CdL(OAc)] · 2 MeOH in DMSO. The evolution of [CdL(OAc)] · 2 MeOH to [$CdL_2$] is also supported by the FAB mass spectrum of the former complex, in which the [$CdL_2$] peak is clearly observed, and by [$CdL_2$Py] having been isolated from a pyridine solution of [CdL(OAc)] · 2 MeOH (vide supra). The fact that the $^{113}$Cd spectrum of [CdL(OAc)] · 2 MeOH shows no separate signal for the $Cd(OAc)_2$ that must be formed if the bispyrazolonate species is the result of symmetrization of [CdL(OAc)], may be due to the $Cd(AcO)_2$ signal being very broad.

## Concluding Discussion

When acetoacetanilide and methylacetoacetate thiosemicarbazones (HTSC$^1$ and HTSC$^2$, respectively) react with cadmium(II) acetate in methanol, an elimination/cyclization process leads to the complexes [CdL(OAc)] · 2 MeOH and [$CdL_2$] · 3 $H_2O$ (HL = 2-[amino(thioxo)methyl]-5-methyl-2,3-dihydro-1*H*-3-pyrazolone). In the case of HTSC$^1$, $^1$H-NMR monitoring in [$D_6$]DMSO at room temperature suggests that the probable course of the reaction is initial formation of [Cd(TSC$^1$)$_2$] followed by gradual release of aniline and concomitant cyclization. Determination of the structures of the ligands HTSC$^1$, HTSC$^2$, and HL by X-ray diffraction showed the structural changes involved in this process.

Recrystallization of the complex [CdL(OAc)] · 2 MeOH from pyridine gave the new compound [$CdL_2$Py] which was also studied by X-ray diffraction. The structural parameters of the trigonal bipyramidal coordination sphere suggest that the N,S-bound $L^-$ ligand and the pyridine ligand both form very strong bonds with the cadmium(II) ion. The coordination modes present in [$CdL_2$] · 3 $H_2O$ and [CdL(OAc)] · 2 MeOH were diagnosed on the basis of their solid state IR spectra and $^1$H-, $^{13}$C-, and $^{113}$Cd-NMR spectra in [$D_6$]DMSO: in solid state, both appear to have polymeric structures, with Cd hexacoordinate in [$CdL_2$] · 3 $H_2O$ and pentacoordinate in [CdL(OAc)] · 2 MeOH. In [$D_6$]DMSO, solvent molecules appear to be included in the coordination sphere of the metal.

On reaction with aqueous trifluoroacetic acid both [$CdL_2$] · 3 $H_2O$ and [CdL(OAc)] · 2 MeOH release the free pyrazolone, which can be easily isolated

## Experimental Section

Thiosemicarbazide (Merck), acetoacetanilide (Merck), acetylacetoacetate (Aldrich), and cadmium acetate (Probus) were used as received. The HTSCs were obtained by the method of Jayasree and Aravindakshan.[5]

**HTSC$^1$:** M.p. 161°C. − $C_{11}H_{13}N_4OS$,: calcd. C 52.78, H 5.43, N 22.39, S 12.82; found C 52.75, H 5.60, N 22.54, S 12.74. − IR (KBr): $\tilde{\nu}$ = 3428 (s), 3268 (vs, b) 3155 (s), [ν(N−H)], 1655 (s), [ν(C=O)], 1595 (vs), [ν(C=N)], 1545 (s), 1248 (m), [ν[−N(H)$C_6H_5$], 1090 (s), 872 (m), [ν(C=S)]. − $^1$H NMR (DMSO): δ = 10.17 [s, 1 H, N(4)*H*], 10.05 [s, 1 H, N(2)*H*], 8.16 [s, 1 H, N(1)$H_2$), 7.62 [s, 1 H, N(1)$H_2$], 7.03 [t, 1 H, $C_6H_5$(*Hp*)], 7.28 [t, 2 H, $C_6H_5$(*Hm*)], 7.57 [d, 2 H, $C_6H_5$(*Ho*)], 3.32 [s, 2 H, C(4)$H_2$], 1.98 [s, 3 H, C(3)$H_3$].

**HTSC$^2$:** M.p. 120°C. − $C_6H_{11}N_3O_2S$,: calcd. C 38.08, H 5.86, N 22.20, S 16.95; found C 38.25, H 6.05, N 22.10, S 17.60. − IR (KBr): $\tilde{\nu}$ = 3402 (vs), 3277 (vs), 3169 (s), [ν(N−H)], 1719 (vs), [ν(C=O)], 1599 (vs), [ν(C=N)], 1440 (m), [δ(−$OCH_3$)], 1246 (s), [ν(C−O)], 1090 (s), 853 (m), [ν(C=S)]. − $^1$H NMR (DMSO): δ = 10.15 [s, 1 H, N(2)*H*], 8.54 [s, 1 H, N(1)$H_2$], 7.60 [s, 1 H, N(1)$H_2$], 3.33 [s, 2 H, C(4)$H_2$], 1.94 [s, 3 H, C(3)$H_3$].

The cyclic ligand **2-[amino(thioxo)methyl]-5-methyl-2,3-dihydro-1*H*-3-pyrazolone (HL)** was originally obtained serendipitously as a by-product of the synthesis of acetoacetanilide thiosemicarbazone; the solid formed when the reaction mixture was refluxed for 7 h recrystallizing from methanol as a mixture of HTSC$^1$ and HL. Diffraction and spectroscopic studies were performed using HL crystals separated by hand under a stereoscopic microscope. Later (vide infra) HL was also obtained by acidification of cadmium(II) complexes. − M.p. 185°C. − $C_5H_7N_3OS$: calcd. C 38.21, H 4.49, N 26.73, S 20.40, found C 38.5, H 4.5, N 26.5, S 21.6. − IR (KBr): $\tilde{\nu}$ = 3269 (vs), 3164 (vs), [ν(N−H)], 1654 (vs), [ν(C=O)], 1592 (vs), 1550 (vs), 1507 (m), [ν(ring)], 1093 (s), 875 (m), [ν(C=S)]. − $^1$H NMR (DMSO): δ = 11.98 [s, 1 H, N(3)*H*], 10.36 [s, 1 H, N(1)$H_2$], 9.66 [s, 1 H, N(1)$H_2$], 5.16 [s, 1 H, C(4)*H*], 2.17 [s, 3 H, C(3)$H_3$].

Analytical data were obtained with a Fisons Instruments EA1108CHNS-O microanalyzer. − $^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker WM-250 or a Bruker AMX-300, and $^{113}$Cd-NMR spectra on a Bruker AMX-500. Chemical shifts are quoted on the δ scale (downfield shifts positive) relative to tetramethylsilane ($^1$H and $^{13}$C NMR) or 0.1 M $Cd(ClO_4)_2$ ($^{113}$Cd NMR). The $^{13}$C-NMR spectra of the thiosemicarbazone ligands HTSC$^1$ and HTSC$^2$ were interpreted on the basis of the chemical shifts, the multiplicity of the signals in the non-proton-decoupled spectra and DEPT-135 experiments, and that of HL on the basis of previous assignments for similar rings.[6] − Infrared spectra were recorded using KBr discs in Mattson Cygnus 100 and Bruker IFS66V spectrometers. − Mass spectra were recorded on a Kratos MS50TC spectrometer. − Melting points were determined in a Büchi apparatus.

**Synthesis of [CdL(OAc)]·2 MeOH:** A solution of HTSC$^1$ (0.50 g, 2 mmol) in methanol (15 mL) was added to a hot solution of $Cd(OAc)_2 \cdot 2\,H_2O$ (0.53 g, 2 mmol) in the same solvent (5 mL). After 4 days stirring, the pale yellow solid formed was filtered out and dried under reduced pressure. − M.p. 198°C. − $C_9H_{17}N_3O_5SCd$: calcd. C 27.6, H 4.3, N 10.7; found C 27.5, H 4.5, N 10.5. − MS (FAB, nitrobenzyl alcohol); *m*/*z* (%): 424 (76) [$CdL_2$], 328 (35) [M − 2 MeOH], 270 (60) [$C_5H_7N_3OSCd$], 140 (97) [$C_5H_7N_3S$], 99 (100) [$C_2H_2N_3S$]. − IR (KBr): $\tilde{\nu}$ = 3410 (m, br), [ν(OH)], 3236 (s, br), [ν(N−H)], 1602 (vs, br), [ν(C=O)], 1602 (vs, br) 1497 (m), [ν(ring)], 757 (m, br), [ν(C=S)]. − $^1$H NMR (DMSO): δ = 11.72 [s, 1 H, N(1)$H_2$], 9.72 [s, 1 H, N(1)$H_2$], 4.67 [s, 1 H, C(4)*H*], 4.10 (c, 2 H, $CH_3OH$), 3.11 (d, 6 H, $CH_3$OH), 2.10 [s, 3 H, C(3)$H_3$], 1.83 (s, 3 H, $CH_3$COO).

**Synthesis of [$CdL_2$]·3 $H_2O$:** A solution of methylacetoacetate thiosemicarbazone (HTSC$^2$, 0.50 g, 2.64 mmol) in methanol (30 mL) was added to a methanolic solution (15 mL) of $Cd(OAc)_2 \cdot 2\,H_2O$ (0.70 g, 2.64 mmol). The mixture was refluxed for 2 h and stirred for a further 12 h. The white solid formed was filtered out and dried under reduced pressure; it decomposed before melting. − $C_{10}H_{18}N_6S_2O_5Cd$: calcd. C 25.1, H 3.8, N 17.6; found C 25.3, H 3.3, N, 17.4. − MS (FAB, nitrobenzyl alcohol); *m*/*z* (%): 425 (32) [M − 3 $H_2O$], 309 (31) [$C_6H_6N_4S_2Cd$], 270 (55) [$C_5H_8N_3OSCd$], 99 (91) [$C_2H_2N_3S$]. − IR (KBr): $\tilde{\nu}$ = 3550 (m), [ν(OH)], 3390 (m), 3223 (m, brs), [ν(N−H)], 1600 (vs, br), [ν(C=O)], 1600 (vs, br) 1498 (m), [ν(ring)], 752 (m, br), [ν(C=S)]. − $^1$H NMR (DMSO): δ = 11.73 [s, 1 H, N(1)$H_2$], 9.70 [s, 1 H, N(1)$H_2$], 4.67 [s, 1 H, C(4)*H*], 1.97 [s, 3 H, C(3)$H_3$]. A small part of the product was recrystallized from pyridine and X-ray measurements and spectral studies were performed on the crystalline product so obtained, [$CdL_2$Py]: IR (KBr): $\tilde{\nu}$ = 3097 (s, br), 2959 [s, br, ν(N−H)], 1629 (vs, br), [ν(C=O)], 1600 (s), 1490 (m), [ν(ring)], 752

Table 3. Selected Crystallographic data for HTSC$^1$, HTSC$^2$, HL, and $CdL_2$Py.

| Compound | HTSC$^1$ | HTSC$^2$ | HL | $CdL_2$Py |
|---|---|---|---|---|
| Empirical formula | $C_{11}H_{14}N_4OS$ | $C_6H_{11}N_3O_2S$ | $C_5H_7N_3OS$ | $C_{15}H_{17}CdN_7O_2S_2$ |
| Formula weight | 250.32 | 189.24 | 157.20 | 503.88 |
| Wavelenght [Å] | 0.71073 | 0.71073 | 1.54184 | 1.54056 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Orthorhombic |
| Spacegroup | *P*-1 (n° 2) | $P2_1/c$ (n° 14) | *P*-1 (n° 2) | $P2_12_12_1$ (n° 19) |
| *a* [Å] | 4.817(1) | 7.5943(12) | 6.1552(8) | 12.1905(6) |
| *b* [Å] | 8.696(1) | 11.6146(13) | 7.721(2) | 12.1915(6) |
| *c* [Å] | 15.469(2) | 10.473(2) | 8.1904(11) | 13.3466(6) |
| α [°] | 97.18(1) | 90 | 82.55(2) | 90 |
| β [°] | 97.351(1) | 91.037(9) | 71.18(2) | 90 |
| γ [°] | 103.21(1) | 90 | 70.80(2) | 90 |
| Volume [Å$^3$] | 617.6(3) | 923.7(2) | 347.81(11) | 1983.6(2) |
| *Z* | 2 | 4 | 2 | 4 |
| $D_{calc}$ [g cm$^{-3}$] | 1.820 | 1.361 | 1.501 | 1.687 |
| Absortion coeffic. [mm$^{-1}$] | 0.25 | 0.317 | 3.592 | 11.014 |
| *F*(000) | 264 | 400 | 164 | 1008 |
| Crystal size [mm] | $0.35_{max}$, $0.26_{min}$ | 0.12 × 0.06 × 0.07 | 0.1 × 0.15 × 0.25 | 0.20 × 0.25 × 0.30 |
| Theta range for data collection [°] | 1−26 | 3−30 | 6−70 | 5−74 |
| Index ranges | −5,5; −10,10; 0,19 | 0,5; 0,16; −14,14 | −7,7; −9,0; −9,9 | −13,15; 0,15; −16−0 |
| Reflections collected | 2499 | 2061 | 1419 | 4665 |
| Independent reflections | 2406 | 1884 | 1315 | 3236 |
| $R_{int}$ | 0.0158 | 0.0355 | 0.0123 | 0.0187 |
| Reflections observed | 1468 | 1389 | 1177 | 3134 |
| Criterion for observation | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_1$ | 0.0443 | 0.0596 | 0.0396 | 0.0270 |
| $R_w$ | 0.1433 | 0.1553 | 0.1042 | 0.0700 |
| Largest diff. peak and hole | 0.274 and −0.373 e·Å$^{-3}$ | 0.309 and −0.372 e·Å$^{-3}$ | 0.243 and −0.306 e·Å$^{-3}$ | 0.390 and −0.663 e·Å$^{-3}$ |

(m, br), [ν(C=S)]. – $^1$H NMR (DMSO): δ = 11.74 [s, 2 H, N(1)$H_2$], 9.70 [s, 2 H, N(1)$H_2$], 8.56 [d, 2 H, $C_5H_5N$ (*Ho*)], 7.76 [t, 1 H, $C_5H_5N$ (*Hp*)], 7.37 [t, 2 H, $C_5H_5N$ (*Hm*)], 4.68 [s, 2 H, C(4)*H*], 2.10 [s, 6 H, C(3)$H_3$].

**X-ray Crystal Structure Determinations:** Data were collected on an Enraf–Nonius CAD-4 diffractometer. The structures were solved using the Patterson method for HTSC[1] and [$CdL_2Py$] and direct methods for HTSC[2]and HL, followed by normal difference Fourier techniques. The H atoms were introduced in calculated positions with fixed C–H distances and isotropic thermal parameters (C–H 0.95 Å; $B_{iso}$ = 4 Å$^2$). The structures were refined by the full-matrix least-squares method (anisotropically for the non-H atoms). Atomic scattering factors were those included in SHELX93.[21] Other programs used were SHELX76[22]and, ORTEP.[23] Crystal and refinement data are listed in Table 3.[24]

**Reactivity of Complexes in Acidic Media:** Preliminary experiments exploring the behaviour of [CdL(AcO)] · 2 MeOH and [$CdL_2$] in acidic aqueous suspensions were performed using $F_3CCOOH$(aq) as proton source. The complexes released free HL, which precipitated and was easily isolated.

## Acknowledgments

Support of these investigations by the Ministerio de Educación y Cultura (Spain) is gratefully acknowledged.

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Received April 29, 1999
[I99154]