Chloride Complexation with Thiosemicarbazone Metal Complexes. A Solid State Study

P. X. García-Reynaldos[a]; S. Hernández-Ortega[a]; R. A. Toscano[a]; J. Valdés-Martínez[a]
[a] Instituto de Química, Universidad Nacional Autónoma de México, México, D.F., México

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P. X. GARCÍA-REYNALDOS, S. HERNÁNDEZ-ORTEGA, R. A. TOSCANO and J. VALDÉS-MARTÍNEZ*

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, Cd., 04510 México, D.F., México

A solid state study of the chloride complexation ability of a series of salicylaldehyde thiosemicarbazone Ni(II) complexes is presented. Complexes of general formula [Ni(5-X-HSalTSC)PPh₃]Cl, where 5-X-HSalTSC⁻ represent the monoanion of 5-X-salicylaldhehyde thiosemicarbazones (with X = MeO, Br, NO₂), were studied in comparison with the analog neutral complex [Ni(5-NO₂-SalTSC)PPh₃]. The crystal structure of the compounds show that the coordinated thiosemicarbazones chelate the choride anions through two N—H hydrogen bonds.

INTRODUCTION

Anions have a wide variety of important chemical roles, 70–75% of the substrates and cofactors involved in biological processes are negatively charged species [1]. Since the publication of the seminal work by Park and Simmons in 1968 on bicyclic diammonium molecules [2], anion coordination and sensing by synthetic receptors has been a growing area in supramolecular chemistry [3–9]. Many of these studies have been done following examples shown by nature, where recognition is mainly based on hydrogen bonding interactions, both in neutral and charged receptors. Therefore the design of most synthetic receptors follows this path, since these interactions promote selective binding through topological complementarity [9]. Much of the work in this field has been done using macrocycles or molecules with multiple binding sites for anion encapsulating [8,10–14]. However, appropriately positioned coordination sites also allow effective anion complexation, such as organic neutral receptors based on thiourea [15–21] and urea [20,22–23] which bind anions selectively and can be used as sensors [19–23] or in organic cationic molecules that combine the action of hydrogen bonding and electrostatic attraction [24–26]. Transition metal complexes are of particular interest, as long as they present useful features in anion complexation. The introduction of a metal center can preorganize hydrogen bonding sites of ureas and thioreas [27–29] and the positive charge generated also favors the interaction with the anion [30–32].

Thiosemicarbazones, TSC, and their metal complexes have suitable characteristics for hydrogen bonding interactions [33–35]. However they remain unexplored as anion receptors. To the best of our knowledge, there are only three studies on anion recognition by Zhang and collaborators using thiosemicarbazones and none on their metal complexes. In their work they report the synthesis of neutral thiosemicarbazones and confirm the hydrogen bonding interaction between the receptors and anions in solution [36–38].

As part of an ongoing research study on the supramolecular chemistry of thiosemicarbazones, we selected salicylaldhehyde thiosemicarbazones, 5-X-H₂SalTSC Ni(II) complexes, where X = MeO, Br, NO₂ (see Fig. 1), in order to study their possible interaction with anions in the solid state. In general, H₂SalTSC's act as terdentate S,N,O-ligands and, depending on the pH, as monoanionic [39–41], dianionic [33–35,42], and in a few cases as neutral ligands [44,45]. With Ni(II) they produce either octahedral species, when a molar ratio of

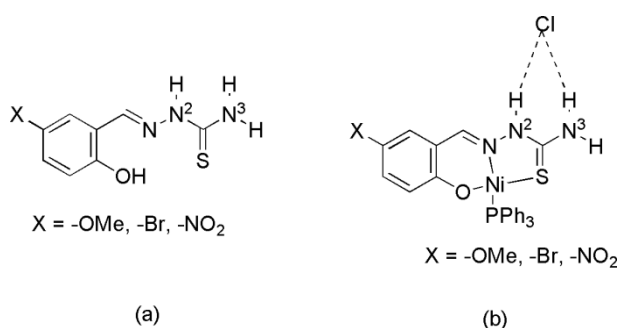*Corresponding author. E-mail: jvaldes@servidor.unam.mx

FIGURE 1 (a) Salicylaldehyde ligands used, (b) Ni(II) metal complexes.

1M:2L is used [43], and square planar when a 1M:1L ratio is utilized [33–35]. In the latter case, insoluble dimers tend to form [42], but the presence of a second monodentate ligand produces soluble square planar complexes [33–35]. To favor the quelation of chlorides, through the interaction of the H atoms on N2 and N4, compounds of general formula $[Ni(5\text{-}X\text{-}HSalTSC)PPh_3]^+$ were selected expecting an interaction as shown in Fig. 1. Phosphines were chosen as the second ligand over the more usual ammines because, under the working conditions, ammines may promote a basic media with the consequent deprotonation of the acidic proton on N2.

These compounds were selected mainly in order to increase the control on the final crystal structure: the cationic complex will avoid the presence of another cation, and additional to ion pairing, the metal center will organize interacting sites favoring anion complexation due to the resulting geometry of the Ni (II) complexes.

In this paper, we present a solid state study of four Ni(II) complexes with salicyldehyde thiosemicarbazones: (5-Methoxysalicylaldehyde thiosemicarbazonato-κ^3 S,N,O)-triphenylphosphine-κ P-nickel(II) chloride ethanol solvate, **1**; (5-bromosalicylaldehyde thiosemicarbazonato-κ^3S,N,O)-triphenylphosphine-κ P-nickel(II) chloride ethanol solvate, **2**; (5-nitrosalicylaldehyde thiosemicarbazonato-κ^3 S,N,O)-triphenylphosphine-κ P-nickel(II) chloride water solvate, **3** and (5-nitrosalicylaldehyde thiosemicarbazonato-κ^3 S,N,O)-triphenylphosphine-κ P-nickel(II), **4**, and analyze their crystal structure in the context of anion complexation.

EXPERIMENTAL SECTION

The commercially available starting materials were used without further purification and solvents were distilled before use. The 5-X-salicylaldehyde-thiosemicarbazones and *bis*(triphenylphosphine)dichloro nickel (II) were obtained as reported elsewere [46].

Preparation of Phosphine(thiosemicarbazonato) Nickel(II) Complexes

[Ni(5-MeO-HSalTSC)PPh₃]Cl·EtOH, 1

An ethanolic solution of the complex *bis*(triphenylphosphine)dichloro nickel (II) (0.319 g, 0.5 mmol/ 10 mL) was added dropwise to a stirring solution of the ligand 5-methoxysalicylaldehyde-thiosemicarbazone, H₂-5-MeO-SalTSC, in dichlorometane (0.113 g, 0.5 mmol/15 mL). The resulting red–brown mixture was stirred for 0.5 h. Over several days at room temperature, the solution gave red-wine prisms of the complex suitable for X-ray diffraction. Yield: 0.272 g (94%). Mp: 143–144°C (dec.).

[Ni(5-Br-HSalTSC)PPh₃]Cl·EtOH, 2

Solutions of *bis*(triphenylphosphine)dichloro nickel (II) (0.319 g, 0.5 mmol/EtOH 10 mL) and 5-bromosalicylaldehyde-thiosemicarbazone, 5-Br-H₂SalTSC, (0.137 g, 0.5 mmol/CH₂Cl₂ 15 mL), were mixed as described above. After several days at room temperature, the solution gave a red prism of the complex suitable for X-ray diffraction. Yield: 0.2965 g (94%). Mp: 233–236°C (dec.).

[Ni(5-NO₂-HSalTSC)PPh₃]Cl·H₂O, 3

For this complex, an ethanolic solution of *bis*(triphenylphosphine)dichloro nickel (II) (0.196 g, 0.3 mmol/EtOH 10 mL) was added to the solution of 5-nitrosalicylaldehyde-thiosemicarbazone, 5-NO₂-H₂SalTSC, (0.072 g, 0.3 mmol) in CH₂Cl₂/HCl (10 mL,10:1). The mixture was left to stand several days at room temperature. The first red crystals obtained were recrystallized from EtOH/CH₂Cl₂/ HCl (10:10:1), to obtain red prisms of the complex suitable for X-ray diffraction. Yield: 0.1472 g (82.5%). Mp: 220°C(dec).

[Ni(5-NO₂-SalTSC)PPh₃], 4

Solutions of *bis*(triphenylphosphine) dichloro nickel (II) (0.327 g, 0.5 mmol) in ethanol (15 mL) and 5-nitrosalicylaldehyde-thiosemicarbazone (0.120 g, 0.5 mmol) in CH₂Cl₂ (10 mL) were combined. The mixture was left to stand several days at room temperature to obtain red prisms of the complex suitable for X-ray diffraction. Yield: 0.231 g (70.8%). Mp (dec, 215°C).

Crystal Structure Determinations

Single crystals of **1–3** were mounted in random orientation on a glass fiber. Crystal data was collected on a Brucker SMART APEX CCD-based

TABLE I   Crystal data and refinement for **1**−**4**

	1	2	3	4
Empirical formula	$C_{29}H_{31}ClN_3NiO_3PS$	$C_{28}H_{28}BrClN_3NiO_2PS$	$C_{26}H_{22}ClN_4NiO_4PS$	$C_{26}H_{21}N_4NiO_3PS$
Formula weight	626.76	675.61	611.66	559.21
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	7.7379(5)	9.5575(7)	9.387(1)	9.5770(6)
b/Å	13.5652(9)	10.7324(8)	11.125(1)	9.6318(6)
c/Å	14.1273(9)	16.626(1)	13.602(1)	13.6426(9)
α/°	100.935(1)	80.679(1)	77.205(2)	87.649(1)
β/°	90.943(1)	94.183(2)	76.753(2)	89.311(1)
γ/°	99.006(1)	108.512(2)	76.816(2)	83.180(1)
V/Å^3	1436.4(2)	1502.7(2)	1324.6(2)	1248.5(1)
Z	2	2	2	2
D_{calc}/g cm^{-3}	1.449	1.493	1.534	1.488
F(000)	652	688	628	576
Crystal Size/mm	$0.09 \times 0.09 \times 0.23$	$0.16 \times 0.34 \times 0.46$	$0.07 \times 0.16 \times 0.17$	$0.30 \times 0.26 \times 0.24$
θMin−Max/°	1.9, 25.0	2.1, 25.0	1.9, 25.0	2.55, 33.04
Npar	370	356	362	331
Tot., Uniq. Data, R(int)	11795, 5031, 0.039	12367, 5280, 0.042	10838, 4667, 0.069	10291, 4401, 0.0305
Observed data				
[I > 2.0 ((I)]	3715	3778	2715	3616
R	0.0374	0.0368	0.0467	0.0315
wR2	0.0554	0.0889	0.0821	0.0760
S	1.00	0.92	0.81	0.951
Min. and Max. Resd. Dens./e Å^{-3}	− 0.34, 0.36	− 0.42, 0.81	− 0.37, 0.56	− 0.230, 0.402

three-circle diffractometer using graphite mono-chromated Mo-Kα (λ = 0.71073 Å) radiation at 293(2) K with SMART software [47]. Data were integrated using SAINT-Plus [47], analytical: face indexed absorption correction was applied, and the space group was determined with XPREP [47]. The structures were solved by direct methods [48] and refined anisotropically with all data by full matrix

TABLE II   Selected bond lengths (Å)and angles (°) of **1**−**4**

|	1	2	3	4
Ni—S	2.1430(8)	2.133(1)	2.138(1)	2.1271(6)
Ni—P	2.2085(8)	2.1869(9)	2.229(1)	2.2201(6)
Ni—O1	1.838(2)	1.845(2)	1.844(3)	1.8572(1)
Ni—N1	1.884(2)	1.879(2)	1.891(3)	1.893(2)
S—C8	1.711(3)	1.712(3)	1.695(4)	1.748(2)
O1—C2	1.309(3)	1.317(4)	1.294(5)	1.302(2)
N1—C7	1.300(3)	1.290(4)	1.294(5)	1.291(2)
N1—N2	1.389(3)	1.388(4)	1.383(5)	1.400(2)
N2—C8	1.322(3)	1.329(5)	1.318(6)	1.295(2)
N3—C8	1.325(4)	1.314(5)	1.331(6)	1.340(3)
S—Ni—P	90.00(3)	92.23(4)	91.72(5)	89.14(2)
S—Ni—O1	175.58(6)	176.64(7)	178.57(9)	174.18(5)
S—Ni—N1	88.24(7)	88.65(8)	87.9(1)	86.97(5)
P—Ni—O1	87.62(5)	84.90(7)	86.88(8)	90.68(4)
P—Ni—N1	178.05(7)	175.21(9)	179.6(1)	165.95(5)
O1—Ni—N1	94.08(8)	94.4(1)	93.5(1)	94.54(6)
Ni—S—C8	97.5(1)	97.5(1)	97.36(2)	96.67(7)
N1—C7—C1	124.6(2)	123.8(3)	124.3(4)	125.4(2)
S—C8—N2	119.2(2)	119.1(2)	120.5(3)	122.8(2)
N2—C8—N3	119.2(2)	118.7(3)	117.2(4)	120.2(2)
S—C8—N3	121.6(2)	122.3(3)	122.3(3)	117.0(2)
Ni—O1—C2	127.5(2)	127.4(2)	128.9(3)	128.2(1)
Ni—N1—C7	127.0(2)	127.0(2)	127.3(3)	125.3(1)
N2—N1—C7	115.5(2)	115.4(3)	114.9(3)	113.2(2)
Ni—N1—N2	117.5(2)	117.5(2)	117.8(2)	121.5(1)
N1—N2—C8	117.5(2)	117.3(3)	116.4(3)	112.2(2)
C7—C1—C2—O1	− 3.8(4)	0.8(5)	1.8(6)	3.60(3)
C2—C1—C7—N1	− 0.2(4)	− 0.9(5)	− 1.6(6)	− 5.40(3)
N2—N1—C7—C1	− 179.3(2)	179.9(3)	− 177.5(4)	− 0.50(3)
C7—N1—N2—C8	− 178.1(2)	175.4(3)	179.0(4)	− 179.3(2)
N1—N2—C8—N3	− 177.9(2)	179.3(3)	− 178.9(3)	179.8(2)
N1—N2—C8—S	2.3(3)	− 0.7(4)	− 0.2(5)	− 1.5(2)
C9—O2—C5—C4	5.1(3)			
O3—N4—C5—C4			0.9(6)	− 0.7(3)
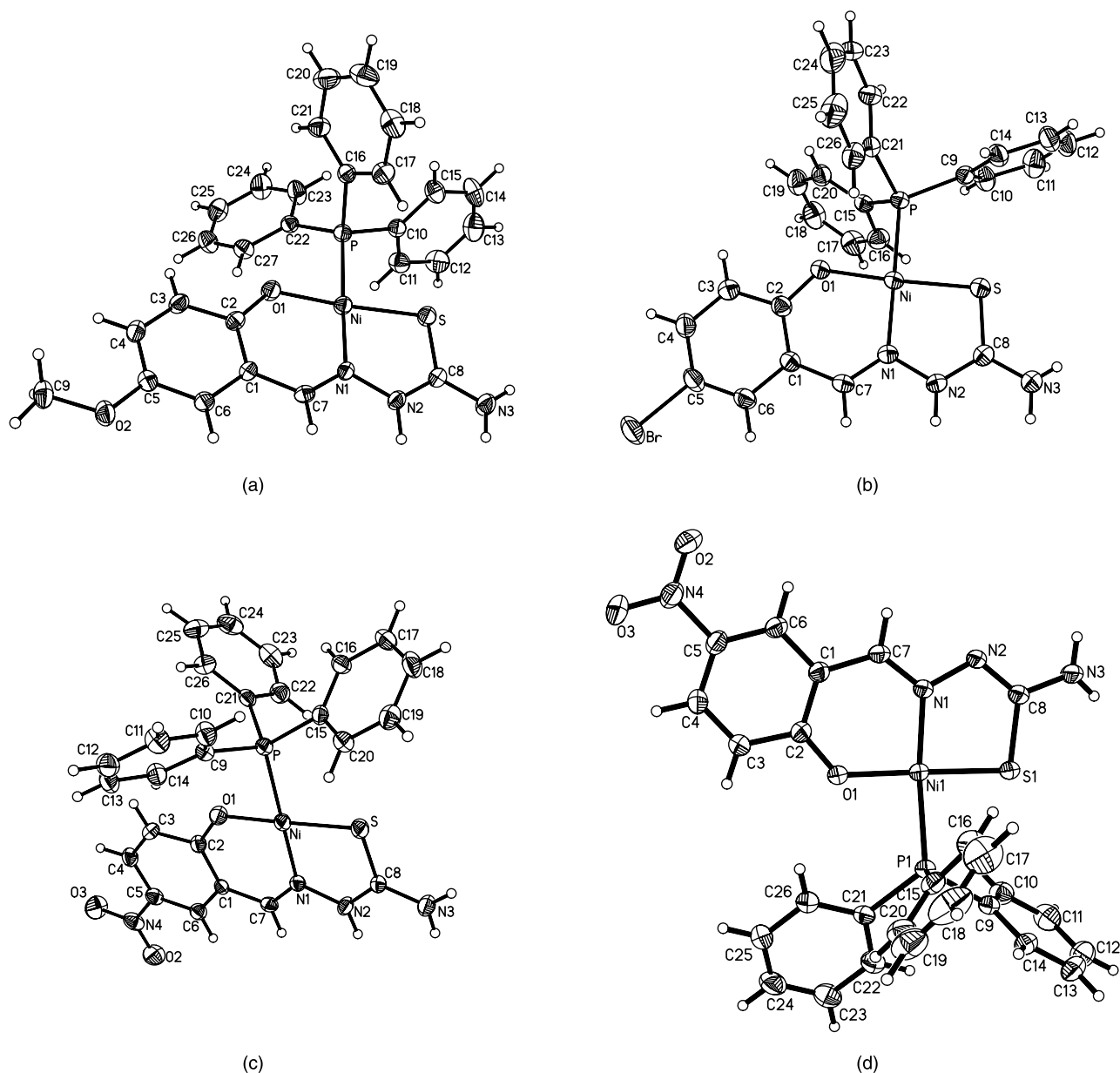
FIGURE 2　Thermal ellipsoid plots (30%) of (a) **1**, (b) **2**, (c) **3**, (d) **4**.

least squares using SHELXL [49]. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions [0.97 Å (CH) and 0.96 Å (CH)] tied to the parent atom with $U_{iso}(H) = 1.5\ U_{eq}$ $C(sp^3)$ and $1.2\ U_{eq}$ for $C(sp^2)$ and refined using the riding model. Hydrogen atoms attached to heteroatoms were localized from the difference electron density map and its positional parameters were refined isotropically for **1** and with fixed $U_{iso}(H) = 1.2\ U_{eq}N$ for **2–4**. Geometric calculations were done using Platon [50]. Table I provides crystallographic details for **1–4** and the molecular geometries and numbering are shown in Fig. 1. CCDC 634952–634955 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam. ac.uk/data/request/cif.

RESULTS

The cationic complexes [Ni(5-X-HSalTSC)PPh$_3$]$^+$, X = MeO, **1** and X = Br, **2**, were obtained directly from the reaction between the *bis*(triphenylphosphine)dichloro nickel (II) and the corresponding salycilaldehyde thiosemicarbazone in ethanol/ dichloromethane solutions. In these compounds the ligands act as monoanionic. Meanwhile when X = NO$_2$ the neutral compound with formula [Ni(5-NO$_2$-SalTSC)PPh$_3$], **4**, was isolated from the direct reaction of the nickel (II) starting material and
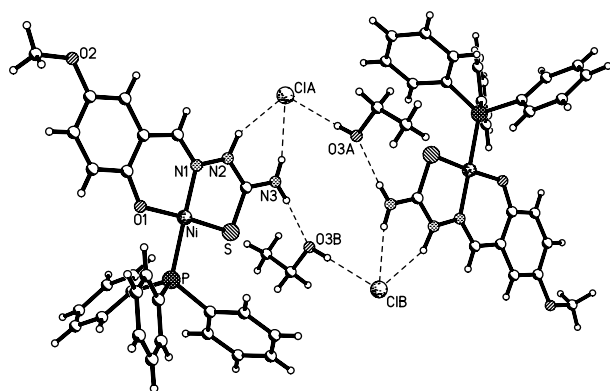
FIGURE 3   Hydrogen bonded anions in **1**.

the ligand 5-NO$_2$-H$_2$SalTSC, which coordinates in this case as dianionic. To obtain the cationic compound, **3**, [Ni(5-NO$_2$-HSalTSC)PPh$_3$]$^+$ it was necessary to add enough HCl to maintain the N2 atom protonated.

The molecular structure of complex cations **1–3** and complex **4** are shown in Fig. 2. Compounds **1–3** are formed by a [Ni(5-X-HSalTSC)PPh$_3$]$^+$ cation a Cl$^-$ anion and solvent molecules (ethanol in **1** and **2** and water in **3**). The Ni atom exhibits a coordination number of four. Due to the loss of the proton on the hydroxy group a monoanionic ligand 5-X-HSalTSC$^-$ is obtained, coordinating to the Ni(II) ion as terdentate *via* the S atom, the azomethine N atom and the phenoxy O atom. The triphenyl phosphine coordinates in the fourth position. The coordination, as indicated by the distances and angles around the metal ion (see Table II), is distorted square planar. The coordinated thiosemicarbazones are more or less planar, as indicated by the corresponding torsion angles, Table II.

Complex **4** is neutral, due to the double deprotonation of the ligand, 5-NO$_2$-SalTSC^{2-}, that loses the hydroxy and the N2 protons. Even though it presents a similar molecular geometry as **1–3**: the ligand acts as terdentate, the phosphine occupies the fourth coordination position, and the geometry around the metal ion is distorted square planar. Moreover, on comparing **4** with the analog cationic compound **3** we found no significant differences in the bond distances, apart from those reflecting the deprotonation of N2, which changes the position of one double bond from C8-S in **3** to N2-C8 in **4**, see Table II.

In the crystal structures of **1–3** the chloride anion forms hydrogen bonds with two N—H's, from N2 and N3, resulting in a ring with graph set R$_2^1$(6) [51], as shown in Figs. 3–5. The ethanol molecules, in **1** and **2**, hydrogen bond to a chloride and to the N3 of the thiosemicarbazone, forming the structures shown in Figs. 3 and 4. In **3** the water molecules form hydrogen bonds with another water molecule and the chloride. These H-bonds combined with
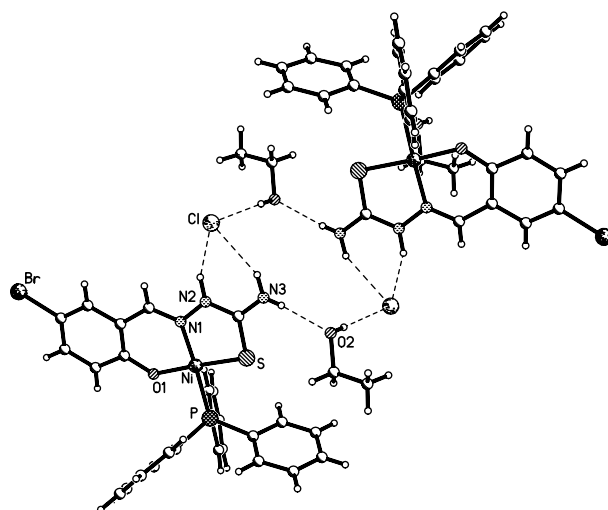

FIGURE 4   Hydrogen bonded anions in **2**.

those formed between the nitro and N3 generate the structures shown in Fig. 5.

The crystal structure of the neutral complex **4**, Fig.6, presents N—H⋯O hydrogen bonds involving the thiosemicarbazone terminal N3—H and one of the O atoms of the nitro group. Through these interactions the molecules are assembled in an infinite chain with graph set *C(11)*. Two chains are linked through the self-complementary N—H⋯N hydrogen bond, R$_2^2$(8), a synthon observed in other Ni(II)-SalTSC compounds with similar structure [33,52], result in a 1D ribbon.

DISCUSSION

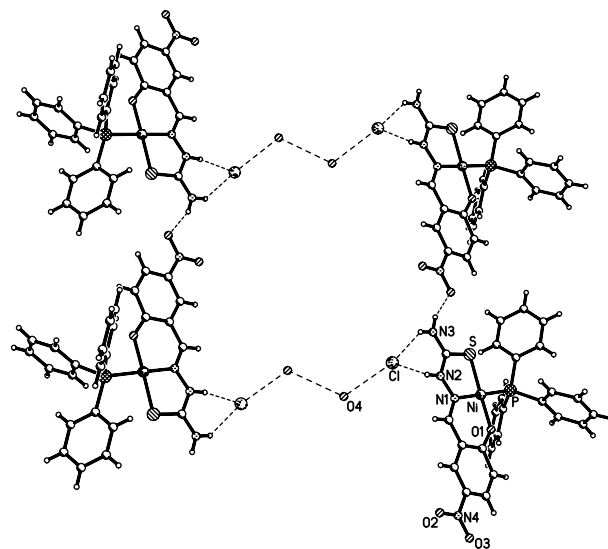The synthetic strategy was successful and the desired square planar compounds were obtained.

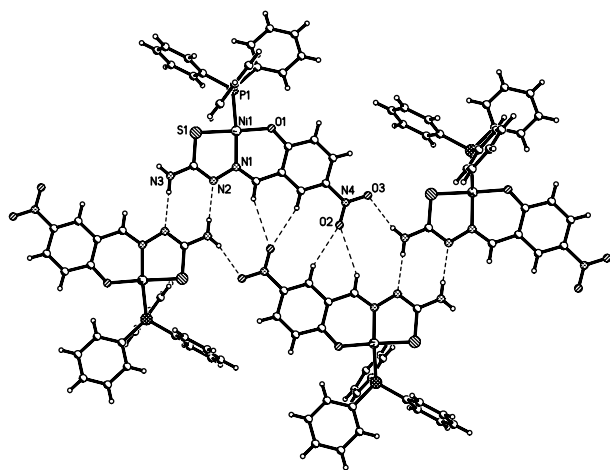FIGURE 5   Hydrogen bonded chlorides in **3**.

FIGURE 6   Hydrogen bonding in **4**.

Although solvation of anions is greatly favored, reproducible H-bonding interactions between the thiosemicarbazones and the chloride were observed in **1–3**, even in the presence of the usually very disruptive water molecules in **3**. Triphenylphosphine was useful to avoid the formation of dimers and the ligand is coordinated at acid pHs as desired. With 5-NO$_2$-H$_2$SalTSC two different complexes were obtained, the desired cationic complex, obtained under acidic conditions, and a neutral complex similar to the one obtained when ammines are used as the second ligand [33–35]. The synthesis of **4** might be due to the electron-attractor properties of the nitro group that favors the deprotonation of the acidic H atom on N2 under the reaction conditions used, making necessary an acid media to obtain the cationic complex.

The solution studies reported by Zhang and collaborators with thiosemicarbazones show no evident binding with chlorides. However, in our study there is an interaction between the metal complex and the chlorides. This suggests, not surprisingly, that the cationic metal complexes increases the anion binding ability of the thiosemicarbazones. In this sense and according to hydrogen bond geometries (Table III), it is possible to classify the charge assisted interactions of these complexes as hydrogen bonds of moderate strength [53], which considering the low basicity of chloride accounts for the behavior of the studied compounds in anion complexation.

It is important to note that when 5-X-H$_2$SalTSC ligands have X = MeO and Br, no influence of these moieties in the supramolecular arrangement of **1** and **2** is observed, but when X = NO$_2$ the ligand acid-base properties are modified and the nitro group, being a strong acceptor for hydrogen bonding, organizes the molecules of **3** and **4**, through N3—H3B$\cdots$O3 interactions. Additionally in **4**, the nitro moiety takes part in C6—H6$\cdots$O2 and C7—H7$\cdots$O2 hydrogen bonds, as shown in Fig. 6. The use of cationic [Ni(HSalTSC$^-$)PPh$_3$]$^+$ complexes was a successful strategy to complex chlorides. In addition, it was possible to control the composition and geometry of the metal complexes all of them being square planar with the 5-X-HSalTSC ligands acting as monoanionic-terdentate and the PPh$_3$ in the forth position. Our results, and those by Zhang, suggest that it is worthwhile integrating thiosemicarbazone moieties and their metal complexes into organic structures designed as hosts for anions.

TABLE III   Hydrogen bond geometries(Å, °)

	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A	Symm transform
1					
N2—H2$\cdots$Cl	0.96(3)	2.21(3)	3.102(2)	154(2)	1 + x,y, − 1 + z
N3—H3A$\cdots$Cl	0.83(3)	2.43(3)	3.203(3)	155(2)	1 + x,y, − 1 + z
N3—H3B$\cdots$O3	0.84(2)	2.00(2)	2.835(4)	172(2)	1 + x,1 + y,z
O3—H3C$\cdots$Cl	0.86(3)	2.27(3)	3.124(2)	168(2)	−x,1 − y,1 − z
2					
O2—H2A$\cdots$Cl1	0.80(5)	2.29(5)	3.072(3)	163(5)	.
N2—H2$\cdots$Cl1	0.95(3)	2.13(3)	3.027(3)	157(3)	−1 + x,y,z
N3—H3A$\cdots$O2	0.71(5)	2.07(4)	2.771(5)	175(6)	1 − x,1 − y,1 − z
N3—H3B$\cdots$Cl1	0.91(4)	2.52(4)	3.319(4)	147(3)	−1 + x,y,z
3					
N2—H2$\cdots$Cl	0.94(4)	2.08(4)	2.984(4)	161(3)	1 + x,y,z
N3—H3A$\cdots$Cl	0.88(4)	2.51(4)	3.250(4)	142(3)	1 + x,y,z
N3—H3B$\cdots$O3	0.90(4)	2.09(4)	2.945(5)	159(4)	1 + x, − 1 + y,z
O4$\cdots$O4			2.205		2 − x, 1 − y, − z
O4$\cdots$Cl			3.17		1 + x, y, z
4					
N3—H3A$\cdots$N2	0.85(3)	2.14(3)	2.986(3)	175(2)	1 − x,1 − y,1 − z
N3—H3B$\cdots$O3	0.80(3)	2.26(3)	3.041(3)	164(3)	1 + x, − 1 + y,z
C6—H6$\cdots$O2	0.93	2.56	3.453(3)	161	−x, 2 − y, 1 − z
C7—H7$\cdots$O2	0.93	2.81	3.650(3)	151	−x, 2 − y, 1 − z

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